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Quantum Optics of Light Scattering

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Quantum Optics of Light Scattering

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Preface

The discovery of Raman scattering unfolded during a period of profound shifts in the perspectives of researchers. Classical physics, once the dominant deterministic framework, was yielding ground to the probabilistic realm of quantum theory. During this transformative period, reluctance to relinquish familiar concepts led to the establishment of new postulates put forward by Niels Bohr. These postulates were expected to restore predictability and comprehension in the ever-evolving landscape of physics.

Yet, the unquestionable validity of these new postulates was not immediately apparent, leading to a greater reliance on mathematical manipulations rather than intuitive physical insight. With time, it became apparent that these new postulates held true only under specific conditions. Interestingly, quantum descriptions remained applicable even when these seemingly steadfast conditions were violated. This extension of the theory revealed that classical and quantum viewpoints were not as divergent as their mathematical frameworks might have suggested.

This cognitive evolution finds a parallel in the development of theories concerning the scattering of electromagnetic waves. Various studies of optical phenomena within the classical physics framework provided only partial insights into observed phenomena. For instance, Rayleigh's theory explained the elastic scattering of light as the radiation of a dipole induced on a molecule by incident radiation, shedding light on the color of the sky. However, this classical theory fell short in explaining the spectral line narrowness observed in the Sun's spectrum, which hinted at the resonant nature of these lines. It was only through the lens of quantum mechanics that a comprehensive understanding of all aspects of this phenomenon emerged.

Certain light scattering phenomena find their explanations exclusively within the realm of quantum mechanics, and these are not confined to obscure phenomena only known to narrow specialists. A prominent illustration is Raman scattering, a fundamental technique for investigating molecular vibrations. Classical explanations have consistently fallen short in their attempts to unravel this phenomenon. To truly

comprehend its intricacies, the application of quantum mechanical concepts is essential from the very outset.

Understanding Raman scattering necessitates the embrace of quantum mechanical concepts like photon absorption and stimulated emission, governed by the interaction of quantized vibrational energy levels with the quantized light field. This coupling leads to characteristic inelastic scattering events, manifest as Stokes and anti-Stokes shifts in the scattered photon energy, directly providing a fingerprint of the molecule's vibrational spectrum. The inability of classical models to predict these shifts underscores the fundamental quantum nature of the interaction. Therefore, a thorough comprehension of Raman scattering necessitates a firm grasp of quantum mechanics, utilizing tools like the quantized electromagnetic field and the vibrational state of molecules.

This book delves into a contemporary exploration of various phenomena in the field of light scattering without diving into the historical evolution of light scattering theory. Whenever feasible, we provide insights into both quantum and semiclassical approaches to these phenomena.

In our descriptions of all optical phenomena, we adopt a unified conceptual platform—the fundamental premise that, for an atom to emit photons, it must interact with an electromagnetic wave and a reservoir of free-state modes. This approach allows us to treat the systems under consideration as open systems, facilitating our understanding of light-scattering phenomena.

Effectively describing open systems requires a meticulous deployment of mathematical and physical tools, including the Heisenberg-Langevin equations and master Lindblad equations. While we have aimed to ensure that the book remains accessible to graduate students and newcomers to the field, we have not shied away from including mathematical details where necessary. As a result, some sections of the book contain lengthy derivations and complex formulas. To balance this, we have placed some derivations within problems. This approach serves a dual purpose: allowing readers to assess their comprehension and mathematical proficiency while keeping the main text uncluttered. At the conclusion of each part of the book, we provide comprehensive solutions to all the problems presented.

Throughout the book, we draw from various concepts in electrodynamics, quantum mechanics, and condensed matter physics. Some of these concepts are not essential for a basic understanding of the text; hence, we have segregated them into Remarks. Omitting these remarks should not hinder reader's comprehension of the core text. However, for readers seeking a deeper grasp of the subject, we recommend reading the remarks in conjunction with the primary text.

Central to our study is the thorough examination of the interaction between molecular electrons and the vibrations of molecular nuclei. We have established that this interaction has a form of the Fröhlich electron-phonon interaction, a concept well established in solid-state physics. This facilitates the bridging of the quantum interpretation of Raman phenomena with its classical counterpart.

Our approach marks a departure from the conventional spectroscopic description, which predominantly operates within the Schrödinger picture. Instead, we pivot to

the Heisenberg picture, which allows for interpreting Raman phenomena as driven by external force oscillations of a quantum system.

Numerous excellent texts and reviews examine various aspects of open quantum systems, exploring topics ranging from quantum thermodynamics and the Lindblad equation to Heisenberg-Langevin operator equations. They offer comprehensive insights into fields as diverse as laser theory, quantum cryptography, and entangled states. However, the application of these advanced approaches has grown increasingly challenging, especially for young researchers aiming to navigate their research domains effectively.

The primary objective of this book is to serve as a bridge between various methodologies for describing the interaction of light with the material environment. It aims to dispel misconceptions and eliminate folklore that has accumulated around the interpretation of light-scattering phenomena. In particular, this book seeks to elucidate the connection between the traditional "spectroscopic" optics based on Fermi's golden rule and contemporary concepts.

We hope that this book will serve as a resource for a diverse audience, including young scientists embarking on the path of exploring the intricacies of light scattering physics, engineers and researchers who employ Raman scattering techniques in their practical work, and experimenters seeking a deeper comprehension of the latest developments in the theory of Rayleigh and Raman scatterings.

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Part I
The Rayleigh Scattering

Chapter 1
Introduction

Probing materials with various particles and analyzing the resulting scattering patterns is a fundamental technique for investigating their internal structure. In studies of the structure of atoms and molecules, photons are usually used as probing particles. The origins of this method can be traced back to the groundbreaking work of Tyndall in 1869 [1], who experimentally observed the light scattered by very small particles.

The theory that explained Tyndall's experiments was developed by Rayleigh [2], who considered the problem of the elastic scattering of an electromagnetic (EM) wave by a subwavelength particle. Rayleigh's theory, employing the principles of classical electrodynamics, attributed the scattering phenomenon to the forced oscillations of the induced polarizability of a subwavelength particle. The developed theory explained the blue hue of the sky by assuming that light was scattered by density fluctuations of a uniform medium [3].

Rayleigh's approach to light scattering encountered some problems. The emergence of new experimental data revealing narrow dark lines in the sun's spectrum [4] did not fit into this theory. These lines suggested an underlying resonance phenomenon, while classical electrodynamics does not predict any resonances when light is scattered by subwavelength particles. This and many other problems were successfully resolved by quantum mechanics, which emerged at the dawn of the twentieth century.

In 1913, Bohr [5] proposed his planetary model of the atom, in which, in the absence of external radiation, electrons can only move along a set of stationary elliptical orbits or shells. Each orbit has a certain energy, and an electron can only have the energy associated with one of the orbits. This starkly contrasts classical electrodynamics, in which electrons moving around the atomic nucleus form a time-varying dipole moment, emit EM waves, and lose energy. In fact, Bohr postulated the existence of discrete stationary states characterized by their own energies. Only under the influence of incident light can an electron transition between orbits by absorbing or emitting a quantum of light. According to Bohr's assumption, the energy of the atom-field system is conserved. Consequently, the energy of the

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quantum of emitted light should precisely match the energy difference between the initial and final states, $\hbar\omega = E_i - E_f$. This explains dark lines in the solar spectrum. Bohr's work was the beginning of quantum mechanics, which emerged as a widely recognized scientific discipline in the early 1930s. Later, such a vision developed into a whole direction in molecular optics – spectroscopy [6].

From the principle of correspondence of quantum-mechanical operators to classical quantities, it follows that in quantum mechanics, the interaction of light with an atom may have a dipole character, as in the classical Rayleigh theory of light scattering.

The quantum operator of the dipole moment is antisymmetric with respect to the change in the sign of the coordinates; therefore, its expectation value of the interaction operator is nonzero only if the initial and final states have different parity. Rayleigh scattering is an elastic process in which the atom must return to its original state after an act of scattering. Thus, the parity of the initial and final wave function is the same, and from the quantum mechanical point of view, the Rayleigh scattering cannot happen. To obtain a nonzero result, the light scattering is treated as a sequence of acts of photon absorption and emission [7, 8]; i.e., it is assumed that during the Rayleigh scattering, the atom passes from the ground state to some intermediate, excited state and then returns to the ground state [9].

The main difficulty of this approach lies in its limitation to the resonant case, where the energy of the incident photon precisely matches the energy difference between the atomic levels, $\hbar\omega_{ext} = \Delta E_{if}$. Generally, a molecule has no eigenstate separated from the ground state by the energy that equals to $\hbar\omega_{ext}$. To resolve this difficulty, *virtual* states and *virtual transitions* were introduced artificially [7, 8, 10]. Throughout the book, we refer to such an approach as the spectroscopic approach.

While the spectroscopic approach to scattering provides a vivid conceptualization of the phenomenon, it harbors an internal inconsistency. As experiments show, the Rayleigh scattering, as an elastic process, after which the atom reverts to its original energy state. To reconcile the theory with experiment, the virtual level should have a very narrow linewidth or an exceptionally long lifetime, which contradicts the assumption of rapid photon reemission [7, 8]. This is why evidence of the existence of *virtual* states has never been found. In this book, we show that modern quantum mechanics allows us to describe the light-scattering phenomena without employing the concept of *virtual* states.

Rabi [11] and Jaynes and Cummings [12] works marked the emergence of a new view on the atom interaction with EM radiation. It was shown that an atom resonantly interacting with a monochromatic mode of incident light neither absorbs nor emits photons – there is only periodic motion from one stationary state to another. This motion involves a continuous, endless energy exchange between the incident field and the atom. This means that the resonant harmonic field cannot cause the atom transition between stationary states.

The theory of open quantum systems showed that an irreversible state change may only happen in an open quantum system, i.e., the system interacting with a reservoir of an infinite number of degrees of freedom [13–18]. In the scattering

problem, it means that in addition to the interaction of an atom with incident light, we have to take into account the interaction with the reservoir of free space modes, which are not included in the incident field. The dynamics of an open quantum system cannot be described by either the Schrödinger equation or the Heisenberg operator equations. Instead, one has to use the Lindblad equation or the Heisenberg-Langevin operator equations.

In this book, we develop a theory of light scattering by atoms, which is based on ideas of open quantum systems. To simplify the math and gain insight into the physical picture of the atom-photon interaction, we model the atom by a two-level system (TLS). This commonly used approximation is valid if only two atomic energy levels involved in the phenomenon under consideration are essential [19].

In Chap. 2, we consider the behavior of a TLS interacting with classical and quantized fields (the Rabi and the Jaynes-Cummings problems, respectively). In both cases, we deal with "closed" quantum systems described by time-dependent Hamiltonians. To describe these systems, we use the following approaches: the "dressed" atom approach, in which the unified states of the atom with a single mode of the EM field are considered [20], and the Bloch formalism based on Floquet's theorem [21]. We show that if the atom interacts with a single monochromatic mode of light, whether the light is classical or quantized, the transition of an atom from one state to another does not occur. Only the endless periodic energy exchange between the atom and the field is possible in such systems.

The third chapter is devoted to "open" quantum systems. In particular, we consider transitions between stationary states of an atom. We show that these transitions are irreversible only if the atom interacts with a reservoir with an infinite number of degrees of freedom. Interaction with such a reservoir is a necessary condition for the atom's transition from one state to another. This is illustrated with the exact Weisskopf-Wigner descriptions of the spontaneous emission of an excited atom [22]. Since it is difficult to deal with a reservoir with many degrees of freedom, approximate approaches need to be used. We discuss the two most popular approaches.

First, in the Schrödinger picture, we introduce the density matrix concept and obtain the Lindblad equation. Using this approach, we consider Fermi's golden rule for the probability of transitions between atomic levels.

Second, in the Heisenberg picture, by eliminating the reservoir variables, we derive the non-Hermitian Heisenberg-Langevin operator equations. These equations contain both dissipative and noise terms but only include the dynamic variables of the system (in our case, it is a dressed atom). Therefore, the equations are much simpler than the initial Hermitian Heisenberg equations for the system and reservoir variables. Using the Heisenberg-Langevin equations allows us to show how an excited open quantum system radiates. To describe this phenomenon, first, we study the relaxation of the systems due to the interaction with the reservoir; then, we find the spectrum of the system dipole moment oscillations and, finally, solve the Heisenberg equations for the free space modes excited by the dipole moment of the system. The perturbation of the reservoir modes is considered as the system's radiation spectrum.

In Chap. 4, we discuss the concept of light coherence. To establish a closer analogy between quantum and classical theories, we consider the correspondence of quantum coherent states of light to coherence of classical EW waves.

In Chap. 5, we employ the Heisenberg-Langevin operator equations to consider a semiclassical description of the Rayleigh scattering. The incident field is treated as classical in this description, but a scatterer is assumed quantum. This leads to the appearance of the off-resonant Mollow triplet.

Finally, in Chap. 6, using the Lindblad master equation, we study the Rayleigh scattering of a quantized field for several formulations of the problem. We start with an incident mode having only one photon. This case corresponds to the Berestetskii-Lifshitz-Pitaevskii approach [8]. Then, we focus on the elementary act of scattering in which the number of photons in the incident mode changes by unity. Placzek [7] was the first to state such a problem. Next, using the Jaynes-Cummings model [12], we consider the CW scattering of a single mode of a quantized field. Finally, we study scattering of light in a coherent state.

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Chapter 2
Exactly Solvable Problems of Atom Interaction with External Electromagnetic Field

In this chapter, we show that in closed Hermitian systems comprised of a finite number of subsystems, each subsystem cannot be in a stationary state. In particular, due to the coupling of an atom with light, the new hybrid states—dressed atom states—arise. In these states, neither the energy of the atom nor the energy of the photons is conserved separately. In a dressed state, there is continuous energy exchange between the atom and the field, and no energy escapes from the system. We illustrate this behavior through the analysis of two exactly solvable problems for forming the dressed atom. These are the interaction of an atom with a single mode of a *classical* EM field (the Rabi problem [1]) and of a *quantized* field (the Jaynes-Cummings problem [2]).

The dressed atom is the simplest quantum system that adequately describes the atom interaction with light. It has become common in quantum optics.

2.1 The Schrödinger and Heisenberg Pictures for Description of Quantum Systems

In this section, we discuss two main approaches describing an atom interaction with an EM field. The first one uses the Schrödinger picture. This is a formulation of quantum mechanics in which the dynamics of a closed quantum system can be described by a wave function $\psi(r,t)$ obeying the Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\psi(r,t)=\hat{H}(r,t)\psi(r,t), \tag{2.1.1}$$

where $\hat{H}(r,t)$ is the system's Hamiltonian.

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Remark 2.1 In quantum mechanics, a system is described by a wave function $\psi(\mathbf{r}, t)$; $|\psi(\mathbf{r}, t)|^2$ has the meaning of the probability density of the particle to be at the point $\mathbf{r}$ at the time t. The initial condition $\psi(r, 0)$ belongs to a space of normalized, square-integrable functions. An inner product of the wave functions $\psi(\mathbf{r}, t)$ and $\varphi(\mathbf{r}, t)$ is defined as

$$\int d^3\mathbf{r}\psi^*(\mathbf{r}, t)\varphi(\mathbf{r}, t)$$

and the norm of the wave function is

$$\|\psi\| = \left(\int d^3\mathbf{r}|\psi(\mathbf{r}, t)|^2\right)^{1/2}.$$

Along with the space of the wave functions, a set of linear operators mapping the wave function's space onto itself is considered. An expectation value of an operator $\hat{A}$ is defined as

$$\left\langle \hat{A} \right\rangle = \int d^3\mathbf{r}\psi^*(\mathbf{r}, t)\hat{A}\psi(\mathbf{r}, t)$$

In addition to the operator $\hat{A}$, there is the Hermitian adjoint operator $\hat{A}^\dagger$ with the property:

$$\int d^3\mathbf{r}\psi(\mathbf{r}, t)\hat{A}^\dagger\varphi^*(\mathbf{r}, t) = \int d^3\mathbf{r}\varphi^*(\mathbf{r}, t)\hat{A}\psi(\mathbf{r}, t).$$

If $\hat{A} = \hat{A}^\dagger$, an operator is referred to as a Hermitian or self-adjoint operator. Further, in quantum mechanics, a Hermitian operator is assigned to any classical physical quantity such as position, momentum, or energy of a particle.

The full set of the eigenfunctions $\{\xi_k(r)\}$ of a Hermitian operator forms the basis of the corresponding Hilbert space [3]. The value of a physical quantity observed in an experiment is equal to one of the eigenvalues of the corresponding operator. The averaged value of the physical quantity observed in a set of identical experiments is equal to the expectation value of the corresponding Hermitian operator.

In quantum mechanics, each physical quantity corresponds to a certain quantum operator (see Remark 2.1). In particular, the energy of the system corresponds to the

Hamiltonian. In the Schrödinger picture, operators do not depend on time.[1] In this picture, values of physical quantities measured in experiment are eigenvalues of the corresponding operator. If the quantum system is in some state described by the wave function $\psi(r,t)$, the average (expectation) value of a physical quantity f corresponding to the quantum operator $\hat{F}$ is defined as

$$\langle f(t)\rangle = \int \psi^*(r,t)\hat{F}\psi(r,t)dV. \tag{2.1.2}$$

The second approach uses the Heisenberg picture, in which the system's time dependency is incorporated into operators. In the Heisenberg picture, expectation values are also defined by Eq. (2.1.2), but now the wave functions are time-independent, while operators depend on time.

Using the Heisenberg picture facilitates the physical interpretation of phenomena. For example, in classical physics, when considering the radiation of light, we deal with the time evolution of a dipole moment. In the Heisenberg picture, we consider the time evolution of the operator of the dipole moment (see Remark 2.2).

Remark 2.2 The Heisenberg quantum mechanical equation for the time-evolution operator is constructed similarly to the evolution equation for classical quantities. In a classical system characterized by the Hamiltonian $H(x,p,t)$, the coordinate x and the momentum p are connected via the Hamiltonian equations $dx/dt = \partial H(x,p,t)/\partial p$ and $dp/dt = -\partial H(x,p,t)/\partial x$; therefore, for an arbitrary function $f(x,p,t)$, one can obtain time-evolution equations by calculating its derivative over time:

$$\begin{aligned}\frac{df(x,p,t)}{dt} &= \frac{\partial f(x,p,t)}{\partial t} + \frac{\partial f(x,p,t)}{\partial x}\frac{dx}{dt} + \frac{\partial f(x,p,t)}{\partial p}\frac{dp}{dt}\\ &= \frac{\partial f(x,p,t)}{\partial t} + \frac{\partial f(x,p,t)}{\partial x}\frac{\partial H(x,p,t)}{\partial p} - \frac{\partial f(x,p,t)}{\partial p}\frac{\partial H(x,p,t)}{\partial x}\\ &= \frac{\partial f(x,p,t)}{\partial t} + \{f(x,p,t), H(x,p,t)\},\end{aligned}$$

where

$$\{A,B\} = \sum_i \left(\frac{\partial A}{\partial x_i}\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial x_i}\right)$$

(continued)

[1] The exceptions are operators, which include classical quantities that are explicitly dependent on time, e.g., a Hamiltonian describing the interaction of a quantum system with classical time-dependent field.

Remark 2.2 (continued)
is called the Poisson bracket. Dirac postulated that to transition from classical quantities to quantum operators, one must replace the Poisson brackets with the commutator of respective operators:

$$\{A, B\} \to (i\hbar)^{-1}\left[\hat{A}, \hat{B}\right].$$

After such a replacement, the equations (the Heisenberg equations), which govern the time dependence of operators, become similar to the corresponding Hamilton equations, which govern the dynamics of classical quantities. Moreover, the dynamics of the expectation values of observable quantities are governed by the same equation (the Ehrenfest theorem [4])**:**

$$\frac{d}{dt}\langle\hat{A}\rangle = \frac{\partial}{\partial t}\langle\hat{A}\rangle + \frac{i}{\hbar}\langle\left[\hat{H}, \hat{A}\right]\rangle.$$

In quantum mechanics, Dirac's bra-ket notations (see Remark 2.3) are often used to describe the system's states. Below, we often employ these notations.

Remark 2.3 **Dirac's bra-ket vectors**. At the beginning of Sect. 2.1, we introduced the Hilbert space in which all wave functions are determined. As a basis of this Hilbert space, we can use a set $\{\xi_k(r)\}$ of eigenfunctions of any Hermitian operator. Therefore, any wave function $\psi(t, r)$ belonging to this Hilbert space can be represented as a linear combination of $\{\xi_k(r)\}$:

$$\psi(t, r) = \sum \psi_k(t)\xi_k(r).$$

The complex functions ψ_k are called probability amplitudes because $P = \psi_k\psi_k^*$ is the probability of finding the system in the state described by the function $\xi_k(r)$.

Dirac introduced convenient notations for describing a quantum system—bra-ket vectors [5]. A column ket vector $|\psi(t)\rangle$ has components $\psi_k(t)$, while a row bra vector $\langle\psi|$ is defined as $\hat{T}|\psi\rangle^*$, where $\hat{T}$ is the transposition operator. The scalar product of the bra and ket vectors is defined as

$$\langle\varphi(t)|\psi(t)\rangle \equiv \sum\nolimits_k \varphi_k{}^*(t)\psi_k(t)$$

One should distinguish the scalar product $\langle\varphi(t)|\psi(t)\rangle$ from the tensor product $|\psi(t)\rangle\langle\varphi(t)|$, which is a direct product of ket and bra vectors and comprises a matrix whose dimension equals $N \times N$, where N is the dimension of the Hilbert

(continued)

Remark 2.3 (continued)
space. The Hermitian operators can also be presented as matrices of the same size with matrix elements $a_{nm} = \int_V \xi_n^* \hat{A} \xi_m dV = \langle \xi_n | \hat{A} | \xi_m \rangle$. These elements are not operators but c-numbers. The action of an operator on ket vector can be written as $|\varphi\rangle = \hat{A}|\psi\rangle$ or $\varphi_n = \sum_m a_{nm} \psi_m$.

The time dependence of the wave function $|\psi(t)\rangle$ may be expressed via the evolution operator $\hat{U}(t, t_0)|\psi(t_0)\rangle$, which, for any $|\psi(t_0)\rangle$, is governed by the equation:

$$i\hbar \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H}(t) \hat{U}(t, t_0). \tag{2.1.3}$$

The validity of this equation can be verified by substituting the expression for $|\psi(t)\rangle$ into Schrödinger Eq. (2.1.1). The Hamiltonian or its parts, e.g., the part describing the interaction with an external classical field, may depend on time explicitly. The solution to this equation with the initial condition $\hat{U}(t_0, t_0) = \hat{1}$ is

$$\hat{U}(t, t_0) = \hat{T} \exp\left(-i/\hbar \int_{t_0}^{t} \hat{H}(t') dt' \right), \tag{2.1.4}$$

where $\hat{T}$ is the time-ordering operator. By employing the operator $\hat{U}(t, t_0)$, one can transition from the Schrödinger picture to the Heisenberg one in which $|\psi_H\rangle = |\psi(t_0)\rangle$. In this part of the book, we label the operators in the Heisenberg picture by the subscript H.

Although, in the Heisenberg picture, expectation values of observables are not defined by Eq. (2.1.2) but by the expression

$$\langle f(t) \rangle_H = \int \psi^*(r, 0) \hat{F}(t) \psi(r, 0) dV, \tag{2.1.5}$$

both expectation values given by Eqs. (2.1.2) and (2.1.5) should be identical. It means that

$$\langle \psi(t) | \hat{A} | \psi(t) \rangle = \langle \psi(t_0) | \hat{U}^\dagger(t_0, t) \hat{A} \hat{U}(t, t_0) | \psi(t_0) \rangle = \langle \psi_H | \hat{A}_H(t) | \psi_H \rangle$$

or

$$\hat{A}_H(t) = \hat{U}^\dagger(t_0, t) \hat{A} \hat{U}(t, t_0). \tag{2.1.6}$$

To find the equation that governs the Heisenberg operators, one has to differentiate the operator $\hat{A}_H(t) = \hat{U}^{\dagger}(t_0, t)\hat{A}_{Schr}\hat{U}(t, t_0)$ over time. After some algebra, we obtain the Heisenberg equation for operators:

$$\frac{d\hat{A}_H}{dt} = \frac{\partial \hat{A}_H}{\partial t} + \frac{i}{\hbar}\left[\hat{H}, \hat{A}_H\right]. \tag{2.1.7}$$

2.2 Hamiltonian of a Two-Level System

In this section, we consider the interaction of an atom modeled by a TLS and a classical monochromatic EM wave having the frequency ω_{ext}.

The functional space of TLS wave functions is two-dimensional. We can choose the excited $|e\rangle$ and the ground $|g\rangle$ eigenstates as basis ket vectors. In the matrix form, $|e\rangle$ and $|g\rangle$ can be represented as

$$|e\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |g\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{2.2.1}$$

Then, the wave function of the TLS can be written as

$$\psi(t) = |\psi(t)\rangle = c_e(t)|e\rangle + c_g(t)|g\rangle. \tag{2.2.2}$$

where $c_e(t)$ and $c_g(t)$ are amplitudes of the probabilities. It is often convenient to represent $|\psi(t)\rangle$ as a column vector:

$$|\psi(t)\rangle = \begin{pmatrix} c_e(t) \\ c_g(t) \end{pmatrix}.$$

Similarly, there are wave functions $\langle\psi|$, which are the Hermitian conjugates for the functions $|\psi(t)\rangle$ (see Remark 2.3). These Hermitian conjugate wave functions can be written as

$$\langle\psi(t)| = \psi^{\dagger}(t) = c_e^*(t)\langle e| + c_g^*(t)\langle g| = \begin{pmatrix} c_e^*(t) & c_g^*(t) \end{pmatrix}$$

where $\begin{pmatrix} c_e^*(t) & c_g^*(t) \end{pmatrix}$ is a row vector and

$$\langle e| = \begin{pmatrix} 1 & 0 \end{pmatrix}, \ \langle g| = \begin{pmatrix} 0 & 1 \end{pmatrix} \tag{2.2.3}$$

are the bra vectors, which form a basis for the TLS wave functions $\langle\psi|$.

In the Schrödinger picture, the operators corresponding to physical quantities are time-independent. Any linear operator acting on the TLS wave function can be represented as a 2×2-matrix of c-numbers, which can be decomposed into a linear combination of the Pauli matrices:

$$\hat{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \ \hat{\sigma}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \ \hat{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

and the unit matrix $\hat{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$. Often, instead of matrices $\hat{\sigma}_1$ and $\hat{\sigma}_2$, it is more convenient to use their linear combinations, which, together with the identity operator, form a basis for operators

$$\begin{aligned} &\hat{\sigma}^\dagger = \frac{1}{2}(\hat{\sigma}_1 + i\hat{\sigma}_2) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \ \hat{\sigma} = \frac{1}{2}(\hat{\sigma}_1 - i\hat{\sigma}_2) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \\ &\hat{D} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \ \hat{I} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \end{aligned} \tag{2.2.4}$$

Note that in the literature on quantum mechanics, the notations $\hat{\sigma}_3$ or $\hat{\sigma}_z$ are usually used instead of the notation $\hat{D}$, while in the literature on laser physics, we encounter the notation $\hat{D}$. In the basis of states $\{|e\rangle, |g\rangle\}$, the operators $\hat{\sigma}^\dagger$, $\hat{\sigma}$, and $\hat{D}$ can be represented as

$$\hat{\sigma}^\dagger = |e\rangle\langle g|, \quad \hat{\sigma} = |g\rangle\langle e|, \quad \hat{D} = |e\rangle\langle e| - |g\rangle\langle g|, \quad I = |e\rangle\langle e| + |g\rangle\langle g|. \tag{2.2.5}$$

From these equations, it follows that $\hat{\sigma}^\dagger|g\rangle = |e\rangle$ and $\hat{\sigma}|e\rangle = |g\rangle$. It implies that the operator $\hat{\sigma}^\dagger$ increases and the operator $\hat{\sigma}$ decreases the number of excitations of the TLS by one, respectively. Therefore, these operators are often referred to as raising and lowering operators of a TLS. Comparing Eqs. (2.2.4) and (2.2.5), one can see that the set of operators

$$\{|e\rangle\langle e|, |g\rangle\langle g|, |g\rangle\langle e|, |e\rangle\langle g|\} \tag{2.2.6}$$

forms a basis for operators in the TLS Hilbert space. Operators (2.2.6) are called transition operators.

Due to the orthogonality of $|e\rangle$ and $|g\rangle$, we have:

$$\hat{\sigma}\hat{\sigma} = \hat{\sigma}^\dagger\hat{\sigma}^\dagger = 0. \tag{2.2.7}$$

Indeed, $\hat{\sigma}^{\dagger}\hat{\sigma}^{\dagger} = |e\rangle\langle g|e\rangle\langle g| = 0$ and $\hat{\sigma}\hat{\sigma} = |g\rangle\langle e|g\rangle\langle e| = 0$; Eq. (2.2.7) can be also checked by using definition (2.2.4) of the matrices $\hat{\sigma}$ and $\hat{\sigma}^{\dagger}$.

Operators (2.2.4) satisfy the commutation relations of the Pauli matrices:

$$\left[\hat{\sigma}^{\dagger}, \hat{\sigma}\right] = \hat{D}, \qquad \left[\hat{\sigma}^{\dagger}, \hat{D}\right] = -2\hat{\sigma}^{\dagger}, \quad \left[\hat{\sigma}, \hat{D}\right] = 2\hat{\sigma} \tag{2.2.8}$$

where square brackets denote a commutator ($\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$).

Wave functions $|g\rangle$ and $|e\rangle$ satisfy Schrödinger equations $\hat{H}_{TLS}|g\rangle = E_g|g\rangle$ and $\hat{H}_{TLS}|e\rangle = E_e|e\rangle$, where E_g and E_e are energies of the TLS ground and excited eigenstates, respectively. Using vectors (2.2.1), one can see that in the basis $\{|g\rangle, |e\rangle\}$, the matrix of $\hat{H}_{TLS}$ has a diagonal form:

$$\begin{pmatrix} E_e & 0 \\ 0 & E_g \end{pmatrix}.$$

In bra-ket notation, the $\hat{H}_{TLS}$ can be presented as

$$\hat{H}_{TLS} = E_e|e\rangle\langle e| + E_g|g\rangle\langle g|, \tag{2.2.9}$$

or taking into account that

$$|g\rangle\langle g| = \begin{pmatrix} 0 \\ 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \frac{1}{2}\left(\hat{I} - \hat{D}\right) \text{ and } |e\rangle\langle e| = \begin{pmatrix} 1 \\ 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \end{pmatrix}$$
$$= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} = \frac{1}{2}\left(\hat{I} + \hat{D}\right)$$

we obtain that

$$\hat{H}_{TLS} = \frac{1}{2}\left(E_e - E_g\right)\hat{D} + \frac{1}{2}\left(E_e + E_g\right)\hat{I} \tag{2.2.10}$$

Since $\hat{\sigma}^{\dagger}\sigma = |e\rangle\langle g||g\rangle\langle e| = |e\rangle\langle e|$, we have $\hat{D} = 2\hat{\sigma}^{\dagger}\sigma - \hat{I} = 2|e\rangle\langle e| - |e\rangle\langle e| - |g\rangle\langle g|$, and one can rewrite Eq. (2.2.10) as

$$\hat{H}_{TLS} = \hbar\omega_{\sigma}\hat{\sigma}^{\dagger}\hat{\sigma} + E_g\hat{I}, \tag{2.2.11}$$

where $\hbar\omega_{\sigma} = E_e - E_g$. Below, unless otherwise is specified, we assume that $E_g = 0$.

2.3 The Hamiltonian of the Two-Level System Interaction with External Electromagnetic Field

In 1788, Lagrange formulated classical mechanics based on the stationary-action principle $\delta S = 0$. The action $S = \int_{t_1}^{t_2} L dt$ was defined through the Lagrangian $L = K - U$, where K and U are the kinetic and potential energies of the system. In 1833, Hamilton reformulated classical mechanics in terms of the total energy of the system. He introduced the Hamiltonian, $H = K + U$, which depends on canonical variables—momenta and generalized coordinates.

EM fields can be described either by four-dimensional tensors or by a single four-dimensional vector comprised of scalar and vector potentials. The latter description is more convenient for forming scalars that could be used to build either Lagrangian or Hamiltonian. The term that describes the interaction between a charged particle and an EM field can be written as a scalar product of the four-dimensional vector comprised of the EM potentials with the four-dimensional vector of the current density of the charged particle [6]. Historically, Hamiltonian mechanics served as a link between classical and quantum mechanics.

To obtain the quantum Hamiltonian of a charged particle interacting with an EM field, following Bohr's correspondence principle, we replace the physical quantities with the corresponding operators:

$$\hat{H} = \frac{1}{2m}\left(\hat{\mathbf{p}} - \frac{e}{c}\hat{\mathbf{A}}\right)^2 + e\hat{\phi} + \hat{V} = \frac{\hat{p}^2}{2m} - \frac{1}{2m}\left(\hat{\mathbf{p}}\cdot\frac{e}{c}\hat{\mathbf{A}} + \frac{e}{c}\hat{\mathbf{A}}\cdot\hat{\mathbf{p}}\right) + \frac{1}{2m}\frac{e^2}{c^2}\left(\hat{\mathbf{A}}\right)^2 + e\hat{\phi} + \hat{V}, \tag{2.3.1}$$

where $\hat{\mathbf{p}} = -i\hbar\nabla$ is the operator of the momentum, the operator $\hat{V}$ is the potential of a static force, e.g., the Coulomb force, $\hat{\phi}$ and $\hat{\mathbf{A}}$ are scalar and vector potentials of the EM field, and e is a particle charge.

Below, subscripts in the EM operators indicate their gauges.

Remark 2.4 **Gauge transformation of EM fields**. The operators of the vector-potential $\hat{\mathbf{A}}$ and the scalar-potential $\hat{\phi}$ do not correspond to any measurable quantities because they are defined up to the gauge transformation with any Hermitian operator $\hat{f}$:

$$\hat{\mathbf{A}} \to \hat{\mathbf{A}} + \nabla\hat{f} = \hat{\mathbf{A}}_{\hat{f}}, \quad \hat{\phi} \to \hat{\phi} - \frac{1}{c}\frac{\partial}{\partial t}\hat{f} = \hat{\phi}_{\hat{f}},$$

(continued)

Remark 2.4 (continued)
This transformation does not affect measurable quantities such as the electric field vector:

$$\hat{\mathbf{E}}_{\hat{f}} = -\nabla\phi_{\hat{f}} - \frac{1}{c}\frac{\partial}{\partial t}\hat{\mathbf{A}}_{\hat{f}} = -\nabla\left(\hat{\phi} - \frac{1}{c}\frac{\partial}{\partial t}\hat{f}\right) - \frac{1}{c}\frac{\partial}{\partial t}\left(\hat{\mathbf{A}} + \vec{\nabla}\hat{f}\right) \equiv \hat{\mathbf{E}},$$

and the magnetic field vector

$$\hat{\mathbf{H}}_{\hat{f}} = \mathrm{curl}\hat{\mathbf{A}}_{\hat{f}} = \mathrm{curl}\left(\hat{\mathbf{A}} + \mathrm{grad}\hat{f}\right) = \hat{\mathbf{H}} + \mathrm{curl}\,\mathrm{grad}\hat{f} \equiv \hat{\mathbf{H}}.$$

which are measurable quantities.

The gauge transformation changes Hamiltonian (2.3.1) (see Remark 2.4) because new terms that explicitly depend on the gauge operators appear. Consequently, the Schrödinger equation also changes. However, after such a Hamiltonian transformation, the new wave function should still correspond to the state physically equivalent to the one described by the unchanged Hamiltonian. In particular, the probability density $P(r,t) = \psi(r,t)\psi^*(r,t) = |\psi(r,t)|^2$ must remain unaffected. Thus, the absolute value of the wave function also should not change. The latter implies that the gauge transformation may only change the wave function phase so that the transformed wave function is obtained by multiplying the initial wave function by a factor $\exp(i\hat{\chi}(r,t))$, where $\hat{\chi}(r,t)$ is a Hermitian operator, i.e.,

$$\psi(r,t) \to \varphi_{\hat{\chi}(r,t)}(r,t) = \exp(i\hat{\chi}(r,t))\psi(r,t), \tag{2.3.2}$$

Our immediate goal is to find the operator $\hat{\chi}(r,t)$ such that the new wave function satisfies the new gauge-transformed Hamiltonian.

For an arbitrary gauge transformation, we have:

$$\begin{aligned}
&\hat{\mathbf{A}} \to \hat{\mathbf{A}} + \nabla\hat{f} = \hat{\mathbf{A}}_f,\\
&\hat{\phi} \to \hat{\phi} - \frac{1}{c}\frac{\partial}{\partial t}\hat{f} = \phi_f,\\
&\psi(r,t) \to \exp(i\hat{\chi}(r,t))\psi(r,t) = \psi_{\hat{f}}(r,t)
\end{aligned} \tag{2.3.3}$$

where $\hat{\chi}(r,t)$ is determined by the requirement that the Schrödinger equation should be invariant with respect to the gauge transformation. In other words, if $\psi(r,t)$ is a solution to the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = \left[\frac{1}{2m}\left(-i\hbar\nabla - \frac{e}{c}\hat{\mathbf{A}}\right)^2 + e\hat{\phi}\right]\psi(\mathbf{r},t), \tag{2.3.4}$$

then $\psi_{\hat{f}}(r,t) = \exp(i\hat{\chi}(r,t))\psi(r,t)$ should be a solution to the Schrödinger equation:

$$i\hbar\frac{\partial\psi_f}{\partial t} = \left[\frac{1}{2m}\left(-i\hbar\nabla - \frac{e}{c}\hat{\mathbf{A}}_f\right)^2 + e\hat{\phi}_f\right]\psi_f. \tag{2.3.5}$$

Thus, our goal is to find the relationship between $\hat{f}(r,t)$ and $\hat{\chi}(r,t)$ that does not change Eq. (2.3.4) when the gauge transformation is applied. The simplest way to achieve this is assuming that, in the quantum case, the gauge transformation is also described by only one function. It means that $\hat{f}(r,t)$ and $\hat{\chi}(r,t)$ differ by the dimensional factor $e/c\hbar$. Let us test this hypothesis by using $\hat{\chi}(r,t) = e\hat{f}(\mathbf{r},t)/c\hbar$ as a trial operator to check whether $\psi_{\hat{f}}(r,t) = \exp\left(\hat{f}(\mathbf{r},t)/c\hbar\right)\psi(r,t)$ satisfies Eq. (2.3.5).

To simplify further mathematical calculations, we prove two lemmas [7].

Lemma 1 If the operators of the vector-potential $\hat{\mathbf{A}}$ and a gauge operator $\hat{f}$ commute for any gauge transformation

$$\left[\hat{\mathbf{A}},\hat{f}\right] = 0, \tag{2.3.6}$$

then in the product $\left(-i\hbar\nabla - \frac{e}{c}\hat{\mathbf{A}}\right)\exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)$, one can change the order of operators by dragging the operator $\exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)$ to the left and simultaneously changing the vector potential to its gauge transformation $\hat{\mathbf{A}}_f = \hat{\mathbf{A}} + \nabla\hat{f}$:

$$\left(-i\hbar\nabla - \frac{e}{c}\hat{\mathbf{A}}\right)\exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)\psi(\mathbf{r},t) = \exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)\left(-i\hbar\nabla - \frac{e}{c}\hat{\mathbf{A}}_{\hat{f}}\right)\psi(\mathbf{r},t) \tag{2.3.7}$$

Proof

$$\begin{aligned}
&\left(-i\hbar\nabla - \frac{e}{c}\hat{\mathbf{A}}\right)\exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)\psi(\mathbf{r},t)\\
&= \left[-i\hbar\nabla\exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)\right]\psi(\mathbf{r},t) - i\hbar\exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)\nabla\psi(\mathbf{r},t)\\
&\quad - \frac{e}{c}\hat{\mathbf{A}}\exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)\psi(\mathbf{r},t)\\
&= \exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)\left(-\frac{e}{c}\nabla\hat{f}(r,t) - i\hbar\nabla - \frac{e}{c}\hat{\mathbf{A}}\right)\psi(\mathbf{r},t)\\
&= \exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)\left(-i\hbar\nabla - \frac{e}{c}\hat{\mathbf{A}}_{\hat{f}}\right)\psi(\mathbf{r},t)
\end{aligned} \tag{2.3.8}$$

Lemma 2 If the conditions of Lemma 1 are fulfilled, then one can change the order of operators in the product $\left(-i\hbar\nabla-\frac{e}{c}\hat{\mathbf{A}}\right)^2\exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)$ by dragging the operator $\exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)$ to the left simultaneously changing the vector potential to its gauge transformation $\hat{\mathbf{A}}_f=\hat{\mathbf{A}}+\nabla\hat{f}$:

$$\begin{aligned}&\left(-i\hbar\nabla-\frac{e}{c}\hat{\mathbf{A}}\right)^2\exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)\psi(\mathbf{r},t)\\&\qquad=\exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)\left(-i\hbar\nabla-\frac{e}{c}\hat{\mathbf{A}}_{\hat{f}}\right)^2\psi(\mathbf{r},t)\end{aligned}\tag{2.3.9}$$

Proof

$$\begin{aligned}&\left(-i\hbar\nabla-\frac{e}{c}\hat{\mathbf{A}}\right)\left\{\left(-i\hbar\nabla-\frac{e}{c}\hat{\mathbf{A}}\right)\exp\left(-i\frac{e}{c\hbar}\hat{f}\right)\psi(r,t)\right\}\\&\quad=\left(-i\hbar\nabla-\frac{e}{c}\hat{\mathbf{A}}\right)\exp\left(-i\frac{e}{c\hbar}\hat{f}\right)\left\{\left(-i\hbar\nabla-\frac{e}{c}\hat{\mathbf{A}}_{\hat{f}}\right)\psi(r,t)\right\}\\&\quad=\exp\left(-i\frac{e}{c\hbar}\hat{f}\right)\left(-i\hbar\nabla-\frac{e}{c}\hat{\mathbf{A}}_{\hat{f}}\right)\left(-i\hbar\nabla-\frac{e}{c}\hat{\mathbf{A}}_{\hat{f}}\right)\psi(r,t)\\&\quad=\exp\left(-i\frac{e}{c\hbar}\hat{f}\right)\left(-i\hbar\nabla-\frac{e}{c}\hat{\mathbf{A}}_{\hat{f}}\right)^2\psi(r,t).\end{aligned}\tag{2.3.10}$$

Substituting $\psi(\mathbf{r},t)=\exp\left(-i\frac{e}{c\hbar}\hat{f}(\mathbf{r},t)\right)\psi_{\hat{f}}(\mathbf{r},t)$ into Eq. (2.3.4), we obtain:

$$\exp\left(-i\frac{e}{c\hbar}\hat{f}\right)\left[i\hbar\frac{\partial\psi_f}{\partial t}+\frac{e}{c}\frac{\partial\hat{f}}{\partial t}\psi_f\right]=\exp\left(-i\frac{e}{c\hbar}\hat{f}\right)\left[\frac{1}{2m}\left(-i\hbar\nabla-\frac{e}{c}\hat{\mathbf{A}}_{\hat{f}}\right)^2+e\phi\right]\psi_f.\tag{2.3.11}$$

After multiplying both sides of Eq. (2.3.11) by $\exp\left(i\frac{e}{\hbar c}\hat{f}\right)$ and moving the term $\left[\frac{e}{c}\frac{\partial\hat{f}}{\partial t}\right]\psi_f$ from the left- to the right-hand side, we obtain that the transformed wave function ψ_f obeys the Schrödinger equation with the EM potentials $\left(\hat{\mathbf{A}}_f,\hat{\phi}_f\right)$:

$$i\hbar\frac{\partial\psi_f}{\partial t}=\left[\frac{1}{2m}\left(-i\hbar\nabla-\frac{e}{c}\hat{\mathbf{A}}_f\right)^2+e\hat{\phi}_f\right]\psi_f.\tag{2.3.12}$$

Here, Eq. (2.3.3) for the gauge transformation of $\hat{\phi}$ has been used. Thus, we have shown that usage of the trial operator $\hat{\chi}(\mathbf{r},t)=(e/\hbar c)\hat{f}(\mathbf{r},t)$ in the gauge transformation leaves the Schrödinger equation gauge invariant. Finally, the gauge transformation (2.3.3) can be written as

$$\begin{aligned}&\hat{\mathbf{A}}\to\hat{\mathbf{A}}+\nabla\hat{f}=\hat{\mathbf{A}}_f,\\&\hat{\phi}\to\hat{\phi}-\frac{1}{c}\frac{\partial}{\partial t}\hat{f}=\phi_f,\\&\psi(r,t)\to\exp\left(i(e/\hbar c)\hat{f}(\mathbf{r},t)\right)\psi(r,t)=\psi_{\hat{f}}(r,t)\end{aligned}\tag{2.3.13}$$

Our next step is finding the transformation in which the local interaction Hamiltonian is written in the gauge-invariant form, $-\hat{\mathbf{d}}\cdot\hat{\mathbf{E}}$ [8]. Such a gauge means that we deal with a dipole approximation, assuming that at the atomic scale, the electric field varies in space slowly ($\omega r_a/c \ll 1$), where r_a is a Bohr radius; we also take into account that at distances comparable to r_a, we can neglect retardation and consider the optical EM fields as quasistatic.

We begin by considering the fields in the radiation gauge that is suitable for the description of the EM field in the free space:

$$\begin{aligned} &\operatorname{div}\hat{\mathbf{A}}_{(R)} = 0, \\ &\phi_{(R)} = 0, \\ &\hat{H}_{(R)} = \frac{1}{2m}\left(-i\hbar\nabla - \frac{e}{c}\hat{\mathbf{A}}_{(R)}\right)^2 + \hat{V}. \end{aligned} \tag{2.3.14}$$

Here and below, we denote the quantities in the radiation gauge with the subscript (R) and those in the dipole gauge with the subscript (dE). The gauge operator that performs such a transition we denote as $\hat{f}_{(dE)}$.

Since $\phi_{(R)} = 0$, we have $\hat{\mathbf{E}} = -\frac{1}{c}\frac{\partial}{\partial t}\hat{\mathbf{A}}_{(R)}$, and for $\mathbf{k}\cdot\mathbf{r}_a \ll 1$, both vector-potential $\hat{\mathbf{A}}_{(R)}$ and the electric field $\hat{\mathbf{E}}$ may be considered as potential fields. Thus, we can choose the gauge function $\hat{f}_{(dE)}$ to vanish the new vector potential[2]:

$$\hat{\mathbf{A}}_{(dE)} = \hat{\mathbf{A}}_{(R)} + \nabla\hat{f}_{(dE)} = 0. \tag{2.3.15}$$

As a consequence of Eq. (2.3.15), we have:

$$\hat{\mathbf{E}} = -\nabla\hat{\phi}_{(dE)} - \frac{1}{c}\frac{\partial}{\partial t}\hat{\mathbf{A}}_{(dE)} = -\nabla\hat{\phi}_{(dE)} \tag{2.3.16}$$

and

$$\hat{\mathbf{E}} = -\nabla\hat{\phi}_{(R)} - \frac{1}{c}\frac{\partial}{\partial t}\hat{\mathbf{A}}_{(R)} = -\frac{1}{c}\frac{\partial}{\partial t}\hat{\mathbf{A}}_{(R)} \tag{2.3.17}$$

Certainly, $\hat{\mathbf{E}}_{(dE)} = \hat{\mathbf{E}}_{(R)}$ because $\hat{\mathbf{E}}$ does not depend on gauge (see Remark 2.4).

Integrating Eq. (2.3.16), we obtain that

$$\hat{\phi}_{(dE)}(\mathbf{r},\mathrm{t}) - \hat{\phi}_{(dE)}(\mathbf{r}_0,\mathrm{t}) = -\int_{\mathbf{r}_0}^{\mathbf{r}} d\mathbf{r}_1\cdot\hat{\mathbf{E}}(\mathbf{r}_1,t) \simeq -\mathbf{d}\cdot\hat{\mathbf{E}}(\mathbf{r}_0,t)/e, \tag{2.3.18}$$

[2] Note that for $\omega r_a/c \ll 1$, the electric and magnetic quasistatic problems are decoupled. No surprise that dealing with electric dipole interaction, we obtain that the magnetic field is zero.

where in the last step, we use that in the dipole approximation $\mathbf{E}(\mathbf{r}_1, t) \simeq \mathbf{E}(\mathbf{r}_0, t)$ and introduce the dipole moment operator $\mathbf{d} = e(\mathbf{r} - \mathbf{r}_0)$. Here $\mathbf{r}_0$ is the location point of the atom nucleus.

Choosing the value $\hat{\phi}_{(dE)}(\mathbf{r}_0, t)$ equal to zero, we can see that in the radiation gauge, the Hamiltonian $\hat{H}_{(R)} = \frac{1}{2m}\left(-i\hbar\nabla - \frac{e}{c}\hat{\mathbf{A}}_{(R)}\right)^2 + \hat{V}$ transforms into the Hamiltonian in the dipole gauge as

$$\hat{H}_{(dE)} = \hat{H}_0 + e\hat{\phi}_{(dE)}(\mathbf{r}, \mathrm{t}) \simeq \hat{H}_0 - \mathbf{d} \cdot \hat{\mathbf{E}}(\mathbf{r}_0, t) \tag{2.3.19}$$

where $\hat{H}_0 = 1/(2m)(i\hbar\nabla)^2 + \hat{V}$ is a part of the Hamiltonian that is independent of EM fields.

Now, we can find the gauge function $f_{(dE)}(\mathbf{r}, t)$. Since $\omega \mathrm{r}_a/c \ll 1$, without losing accuracy, Eq. (2.3.18) can be rewritten as

$$\begin{aligned}\hat{\phi}_{(dE)}(\mathbf{r}, \mathrm{t}) - \hat{\phi}_{(dE)}(\mathbf{r}_0, \mathrm{t}) &= -\int_{\mathbf{r}_0}^{\mathbf{r}} d\mathbf{r}_1 \cdot \hat{\mathbf{E}}(\mathbf{r}_1, t) \simeq -\left(\hat{\mathbf{E}}(\mathbf{r}, t) \cdot \mathbf{r} - \hat{\mathbf{E}}(\mathbf{r}_0, t) \cdot \mathbf{r}_0\right) \\ &= \frac{\partial}{c\partial t}\left(\hat{\mathbf{A}}_{(R)}(\mathbf{r}, t)\mathbf{r} - \hat{\mathbf{A}}_{(R)}(\mathbf{r}_0, t) \cdot \mathbf{r}_0\right).\end{aligned} \tag{2.3.20}$$

This equality is obtained by taking into account that $\hat{\mathbf{E}} = -\frac{1}{c}\frac{\partial}{\partial t}\hat{\mathbf{A}}_{(R)}$ (see Eq. (2.3.17)).

By the definition of the gauge transformation, we have:

$$\hat{\phi}_{(dE)}(\mathbf{r}, t) = \hat{\phi}_{(R)}(\mathbf{r}, t) - \frac{1}{c}\frac{\partial}{\partial t}\hat{f}_{(dE)}(\mathbf{r}, t) = -\frac{1}{c}\frac{\partial}{\partial t}\hat{f}_{(dE)}(\mathbf{r}, t)$$

and

$$\hat{\phi}_{(dE)}(\mathbf{r}, t) - \hat{\phi}_{(dE)}(\mathbf{r}_0, t) = -\frac{1}{c}\left(\frac{\partial}{\partial t}\hat{f}_{(dE)}(\mathbf{r}, t) - \frac{1}{c}\frac{\partial}{\partial t}\hat{f}_{(dE)}(\mathbf{r}_0, t)\right) \tag{2.3.21}$$

Finally, we arrive at the following equality:

$$-\frac{1}{c}\frac{\partial}{\partial t}\left(\hat{f}_{(dE)}(\mathbf{r}, t) - \frac{\partial}{\partial t}\hat{f}_{(dE)}(\mathbf{r}_0, t)\right) \simeq \frac{\partial}{c\partial t}\left(\hat{\mathbf{A}}(\mathbf{r}, t)\mathbf{r} - \hat{\mathbf{A}}(\mathbf{r}_0, t) \cdot \mathbf{r}_0\right) \tag{2.3.22}$$

or

$$\hat{f}_{(dE)}(\mathbf{r}, t) = -\hat{\mathbf{A}}_R(\mathbf{r}, t)\mathbf{r}$$

This kind of calibration operator allows us to check our assumption about the commutation of the vector-potential operator and the gauge operator:

$$\left[\hat{f}^{(dE)}(\mathbf{r}_0,t),\hat{\mathbf{A}}_R(\mathbf{r}_0,t)\cdot(\mathbf{r}-\mathbf{r}_0)\right]=0.$$

Now, in product (2.3.11), one can change the order of the factors and treat operators as c-functions.

The size of an atom r_{at} is much smaller than the optical wavelength λ. Therefore, for the interaction Hamiltonian of the TLS with an external field, in the leading order of the small parameter r_{at}/λ, we can use the dipole approximation $\hat{H}_{\text{int}}=-\hat{\mathbf{E}}\cdot\hat{\mathbf{d}}$ (details of the derivation can be found in Ref. [3]), where $\hat{\mathbf{d}}$ is the TLS dipole moment operator. The parity of the states $|e\rangle$ and $|g\rangle$ warrants that $\mathbf{d}_{eg}=\langle e|\mathbf{d}|g\rangle=\langle g|\mathbf{d}|e\rangle=\mathbf{d}_{ge}$, while $d_{ee}=d_{gg}=0$. Thus, the matrix for the dipole moment operator is off-diagonal and symmetric. Using matrices (2.2.4), we can express this operator as

$$\hat{\mathbf{d}}=\mathbf{d}_{eg}\hat{\sigma}^{\dagger}+\mathbf{d}_{ge}\hat{\sigma}\quad\text{or}\quad\hat{\mathbf{d}}=\mathbf{d}_{eg}\left(\hat{\sigma}+\hat{\sigma}^{\dagger}\right)\tag{2.3.23}$$

To summarize, in the dipole approximation, the interaction Hamiltonian of the TLS with an external classical field of the frequency ω_{ext} ($\mathbf{E}_{ext}(\exp(-i\omega_{ext}t)+\exp(i\omega_{ext}t))/2$) is

$$\hat{H}_{\text{int}}=-\hat{\mathbf{d}}\cdot\hat{\mathbf{E}}=\hbar\Omega_{ext}(\exp(-i\omega_{ext}t)+\exp(i\omega_{ext}t))\left(\hat{\sigma}+\hat{\sigma}^{\dagger}\right).\tag{2.3.24}$$

where $\Omega_{ext}=-\mathbf{d}_{eg}\cdot\mathbf{E}_{ext}/2\hbar$ is called the Rabi frequency for the interaction of TLS with the classical EM field.

2.4 The Rabi Cycle in the Heisenberg Picture

In classical mechanics, it is impossible to create two identical objects, while in the quantum world, it is commonplace. All electrons and protons are identical among themselves. This is possible only if the parameters that determine a micro-object have discrete values. In particular, two unexcited hydrogen atoms are identical, just as two excited to the same levels. Consequently, the frequencies characterizing transitions between ground and excited states of identical atoms are also identical.

According to this, it may seem that quantum mechanics is doomed to only study transitions between discrete states. However, Rabi showed that the population of the excited state of the TLS, under the action of an external monochromatic field, can perform smooth oscillations. The solution to this problem in the Schrödinger picture can be found in many textbooks on quantum mechanics (see also Problem 1.1). Below, for pedagogical purposes, we present the solution to this problem in the Heisenberg picture.

The transition from the Schrödinger picture to the Heisenberg picture can be done by applying unitary transformation (2.1.4). It is important that the evolution operator $U(t,t_0)$ commutes with the Hamiltonian. It means that Hamiltonians are the same in

the Heisenberg and Schrödinger pictures. We illustrate this by considering the reduced Hamiltonian describing the TLS interaction with the classical field.

Recall that $\hat{\mathbf{d}} = \mathbf{d}_{eg}\left(\hat{\sigma} + \hat{\sigma}^{\dagger}\right)$. In what follows, we assume that the dipole polarization of the atom is of spherical symmetry. Then, the polarization direction is the same as the direction of the electric field so that $\Omega_{ext} = -d_{eg}E_{ext}/2\hbar$. Thus

$$\hat{H}_{Schr} = \hat{H}_{TLS} - \hat{\mathbf{d}} \cdot \hat{\mathbf{E}} \approx \hbar\omega_{\sigma}\hat{\sigma}^{\dagger}\hat{\sigma} + \hbar\Omega_{ext}\left(\hat{\sigma} + \hat{\sigma}^{\dagger}\right)[\exp(-i\omega_{ext}t) + \exp(i\omega_{ext}t)]. \tag{2.4.1}$$

In the Heisenberg picture, using Eq. (2.1.6), we obtain:

$$\begin{aligned}
\hat{H}_H &= \hat{U}^{\dagger}(t_0,t)\hat{H}_{Schr}\hat{U}(t,t_0) = \hbar\omega_{\sigma}\hat{U}^{\dagger}(t_0,t)\hat{\sigma}\hat{U}(t_0,t)\hat{U}^{\dagger}(t,t_0)\hat{\sigma}^{\dagger}\hat{U}(t_0,t) \\
&+ \hbar\Omega\left(\hat{U}^{\dagger}(t_0,t)\hat{\sigma}^{\dagger}\hat{U}(t_0,t)e^{-i\omega_{ext}t} + \hat{U}^{\dagger}(t_0,t)\hat{\sigma}\hat{U}(t_0,t)e^{i\omega_{ext}t}\right) \\
&+ \hbar\Omega\left(\hat{U}^{\dagger}(t_0,t)\hat{\sigma}^{\dagger}\hat{U}(t_0,t)e^{i\omega_{ext}t} + \hat{U}^{\dagger}(t_0,t)\hat{\sigma}\hat{U}(t_0,t)e^{-i\omega_{ext}t}\right) \\
&= \hbar\omega_{\sigma}\hat{\sigma}_H^{\dagger}\hat{\sigma}_H + \hbar\Omega_{ext}\left(\hat{\sigma}_H^{\dagger} + \hat{\sigma}_H\right)\left(e^{i\omega_{ext}t} + e^{-i\omega_{ext}t}\right).
\end{aligned}$$

Operators $\hat{\sigma}^{\dagger}$ and $\hat{\sigma}$ change under transformation (2.1.6). In the Heisenberg picture, these operators depend on time, and their dynamics is determined by Heisenberg equation (2.1.7). Unlike the Schrödinger picture, in the Heisenberg picture, these operators evolve with time; therefore, in both pictures, they are identical in the initial moment only. So, in the Heisenberg picture, the operators $\hat{\sigma}_H^{\dagger}(t)$ and $\hat{\sigma}_H(t)$ do not have the form of Eq. (2.2.4) in an arbitrary moment of time. However, any linear operator can still be presented as a linear combination of the operators $\left\{\hat{\sigma}_H, \hat{\sigma}_H^{\dagger}\hat{D}_H, \hat{I}\right\}$.

Now, we discuss the TLS interaction with the classical field within the framework of the Heisenberg picture. This discussion is mainly instructional.

The Hamiltonian of a TLS interacting with an external classical field is equal to the sum of Hamiltonians (2.2.11) and (2.3.24); therefore, the Heisenberg equations take the form (see Problem 1.2):

$$\begin{aligned}
\frac{d\hat{\sigma}_H}{dt} &= -i\omega_{\sigma}\hat{\sigma}_H + i\Omega_{ext}\left(\hat{\sigma}_H^{\dagger}\hat{\sigma}_H - \hat{\sigma}_H\hat{\sigma}_H^{\dagger}\right)\exp(-i\omega_{ext}t) + i\Omega_{ext}\left(\hat{\sigma}_H^{\dagger}\hat{\sigma}_H - \hat{\sigma}_H\hat{\sigma}_H^{\dagger}\right)\exp(i\omega_{ext}t) \\
&= -i\omega_{\sigma}\hat{\sigma}_H + i\Omega_{ext}\left[\hat{\sigma}_H^{\dagger}, \hat{\sigma}_H\right]\exp(-i\omega_{ext}t) + i\Omega_{ext}\left[\hat{\sigma}_H^{\dagger}, \hat{\sigma}_H\right]\exp(i\omega_{ext}t),
\end{aligned} \tag{2.4.2}$$

$$\frac{d\hat{\sigma}_H^\dagger}{dt} = i\omega_\sigma \hat{\sigma}_H^\dagger - i\Omega_{ext}\left(\hat{\sigma}_H^\dagger \hat{\sigma}_H - \hat{\sigma}_H \hat{\sigma}_H^\dagger\right)\exp(i\omega_{ext}t) - i\Omega_{ext}\left(\hat{\sigma}_H^\dagger \hat{\sigma}_H - \hat{\sigma}_H \hat{\sigma}_H^\dagger\right)\exp(-i\omega_{ext}t)$$
$$= i\omega_\sigma \hat{\sigma}_H^\dagger - i\Omega_{ext}\left[\hat{\sigma}_H^\dagger, \hat{\sigma}_H\right]\exp(i\omega_{ext}t) - i\Omega_{ext}\left[\hat{\sigma}_H^\dagger, \hat{\sigma}_H\right]\exp(-i\omega_{ext}t). \tag{2.4.3}$$

System of Eqs. (2.4.2) and (2.4.3) is nonlinear because it contains the products $\hat{\sigma}_H^\dagger \hat{\sigma}_H$ and $\hat{\sigma}_H \hat{\sigma}_H^\dagger$. These products form the Hermitian nonlinear operator $\hat{D}_H = \hat{\sigma}_H^\dagger \hat{\sigma}_H - \hat{\sigma}_H \hat{\sigma}_H^\dagger = \left[\hat{\sigma}_H^\dagger, \hat{\sigma}_H\right]$, which has the meaning of the atomic population inversion. Indeed, in the Schrödinger picture, $|\psi\rangle = c_e|e\rangle + c_g|g\rangle$ and

$$\langle \hat{D} \rangle = \langle \hat{\sigma}^\dagger \hat{\sigma} \rangle - \langle \hat{\sigma} \hat{\sigma}^\dagger \rangle = |c_e|^2 - |c_g|^2. \tag{2.4.4}$$

Using the operator $\hat{D}_H$ makes system (2.4.2)–(2.4.3) linear for the variables $\left\{\hat{\sigma}_H, \hat{\sigma}_H^\dagger, \hat{D}_H\right\}$. To complete this system, we have to derive an equation for the operator $\hat{D}_H$. Using Eq. (2.1.7) and taking into account that $\hat{\sigma}_H^\dagger \hat{\sigma}_H = \left(1 + \hat{D}_H\right)/2$, we obtain (Problem 1.2):

$$\frac{d\hat{D}_H}{dt} = 2i\Omega_{ext}\left(\hat{\sigma}_H - \hat{\sigma}_H^\dagger\right)\left(\exp(i\omega_{ext}t) + \exp(-i\omega_{ext}t)\right). \tag{2.4.5}$$

System of Eqs. (2.4.2)–(2.4.5) is closed and linear; the coefficients in this system are time-dependent. To simplify the system, we introduce auxiliary operators $\widehat{\tilde{\sigma}}_H(t) = \hat{\sigma}_H \exp(i\omega_{ext}t)$ and $\widehat{\tilde{\sigma}}_H^\dagger(t) = \hat{\sigma}_H^\dagger(t)\exp(-i\omega_{ext}t)$. These operators satisfy the following linear system:

$$\frac{d\widehat{\tilde{\sigma}}_H}{dt} = i\Delta_\omega \widehat{\tilde{\sigma}}_H + i\Omega_{ext}\hat{D}_H + i\Omega_{ext}\hat{D}_H \exp(2i\omega_{ext}t) \tag{2.4.6}$$

$$\frac{d\widehat{\tilde{\sigma}}_H^\dagger}{dt} = -i\Delta_\omega \widehat{\tilde{\sigma}}_H^\dagger - i\Omega_{ext}\hat{D}_H - i\Omega_{ext}\hat{D}_H \exp(-2i\omega_{ext}t) \tag{2.4.7}$$

$$\frac{d\hat{D}_H}{dt} = 2i\Omega_{ext}\left(\widehat{\tilde{\sigma}}_H - \widehat{\tilde{\sigma}}_H^\dagger\right) + 2i\Omega_{ext}\left(\widehat{\tilde{\sigma}}_H \exp(-2i\omega_{ext}t) - \widehat{\tilde{\sigma}}_H^\dagger \exp(2i\omega_{ext}t)\right) \tag{2.4.8}$$

where $\Delta_\omega = \omega_{ext} - \omega_\sigma$ is the detuning of the external field frequency from the TLS transition frequency. Systems (2.4.6)–(2.4.8) with arbitrary initial conditions, $\widehat{\tilde{\sigma}}_H(0)$, $\widehat{\tilde{\sigma}}_H^\dagger(0)$, and $\widehat{\tilde{D}}_H(0)$ can be solved analytically.

Further, throughout the book, we use the rotating wave approximation, in which the terms proportional to $\exp(\pm 2i\omega_{ext}t)$ are neglected. This approximation is justified when $|\omega_{ext} - \omega_\sigma| \ll \omega_{ext}, \omega_\sigma$ and $\Omega_{ext} \ll \omega_\sigma$. When the latter inequality is satisfied, in Eqs. (2.4.6)–(2.4.8), the terms proportional to $\exp(\pm 2i\omega_{ext}t)$ are fast-oscillating compared to all other terms. It can be shown [9, 10] that these terms give

contribution to the solution of Eqs. (2.3.30)–(2.3.32) that is of the order $(\Omega/\omega_\sigma)^2$ (the so-called Bloch-Siegert shift) compared to the contribution to the solution coming from non-oscillating terms. When $|\omega_{ext} - \omega_\sigma| \ll \omega_{ext}$, ω_σ and $\Omega_{ext} \ll \omega_\sigma$, this shift can be neglected. Neglecting the terms proportional to $\exp(\pm 2i\omega_{ext}t)$ results in the following equations:

$$\frac{d\widehat{\widetilde{\sigma}}_H}{dt} = i\Delta_\omega \widehat{\widetilde{\sigma}}_H + i\Omega_{ext}\hat{D}_H \tag{2.4.9}$$

$$\frac{d\widehat{\widetilde{\sigma}}_H^\dagger}{dt} = -i\Delta_\omega \widehat{\widetilde{\sigma}}_H^\dagger - i\Omega_{ext}\hat{D}_H \tag{2.4.10}$$

$$\frac{d\hat{D}_H}{dt} = 2i\Omega_{ext}\left(\widehat{\widetilde{\sigma}}_H - \widehat{\widetilde{\sigma}}_H^\dagger\right) \tag{2.4.11}$$

It is worth emphasizing that neglecting the fast-oscillating terms in Eqs. (2.4.6)–(2.4.8) is equivalent to neglecting the terms proportional to $\hat{\sigma}_H \exp(-i\omega_{ext}t)$ and $\hat{\sigma}_H^\dagger \exp(i\omega_{ext}t)$ in the interaction Hamiltonian (2.3.24). In other words, it means that in the rotating wave approximation, we deal with the Rabi Hamiltonian:

$$\hat{H}_{Rabi} = \hbar\omega_\sigma \hat{\sigma}^\dagger\hat{\sigma} + \hbar\Omega_{ext}\left(\hat{\sigma}_H^\dagger \exp(-i\omega_{ext}t) + \hat{\sigma}_H \exp(i\omega_{ext}t)\right). \tag{2.4.12}$$

As we mentioned in the introduction, Rabi analytically showed that for $\Delta = 0$, a single monochromatic mode of a classical EM field cannot irreversibly excite an atom. Instead of the atomic transition to the excited state, the atom state oscillates between ground and excited states with the doubled Rabi frequency. During this process, the amplitude of the classical EM wave is assumed to be unchanged. Tracing the energy exchange between the atom and the field is difficult. The atomic energy is not conserved during the Rabi cycle. This is not surprising because Hamiltonian (2.4.12) depends on time.

For $\Delta_\omega = 0$, system (2.4.9)–(2.4.11) is reduced to

$$\frac{d^2\hat{D}_H}{dt^2} + 4\Omega_{ext}^2\hat{D}_H = 0.$$

Thus, for $\Delta_\omega = 0$, the operator $\hat{D}(t)$ exhibits the Rabi oscillations with the frequency 2Ω.

For nonzero detuning $\Delta_\omega \neq 0$, system (2.4.9)–(2.4.11) can also be solved. The eigenfrequencies for this linear system are $\pm 2\Omega_\Delta$ and 0 [11–13]. The quantity $2\Omega_\Delta = \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}$ is the frequency of the population inversion oscillation in the absence of resonance. The general solution to this system is a linear combination of the eigenvectors multiplied by exponents with corresponding eigenfrequencies. The coefficients are determined by the initial conditions $\hat{\sigma}_H(0)$, $\hat{\sigma}_H^\dagger(0)$, and $\hat{D}_H(0)$ (see Problem 1.3). This solution has the form:

$$\hat{\sigma}_H(t) = \left[\Omega_{ext}^2/2\Omega_\Delta^2 + \left(1 - \Omega_{ext}^2/2\Omega_\Delta^2\right)\cos(2\,\Omega_\Delta t) + (i\Delta_\omega/2\Omega_\Delta)\sin(2\,\Omega_\Delta t)\right] \times \exp(-i\omega_{ext}t)\hat{\sigma}_H(0) + \left(\Omega_{ext}^2/2\Omega_\Delta^2\right)(1 - \cos(2\Omega_\Delta t))\exp(-i\omega_{ext}t)\hat{\sigma}_H^\dagger(0) + \left[\left(\Delta_\omega\Omega_{ext}/4\Omega_\Delta^2\right)(\cos(2\Omega_\Delta t) - 1) + (i\Omega_{ext}/2\Omega_\Delta)\sin(2\Omega_\Delta t)\right] \times \exp(-i\omega_{ext}t)\hat{D}_H(0) \tag{2.4.13}$$

$$\hat{\sigma}_H^\dagger(t) = \left(\Omega_{ext}^2/2\Omega_\Delta^2\right)(1 - \cos(2\Omega_\Delta t))\exp(i\omega_{ext}t)\hat{\sigma}_H(0) + \Big[\Omega_{ext}^2/2\Omega_\Delta^2 + \left(1 - \Omega_{ext}^2/2\Omega_\Delta^2\right)\cos(2\,\Omega_\Delta t) - (i\Delta_\omega/2\Omega_\Delta)\sin(2\,\Omega_\Delta t)\Big]\exp(i\omega_{ext}t)\hat{\sigma}_H^\dagger(0) + \left[\left(\Delta_\omega\Omega_{ext}/4\Omega_\Delta^2\right)(\cos(2\Omega_\Delta t) - 1) - (i\Omega_{ext}/2\Omega_\Delta)\sin(2\Omega_\Delta t)\right]\exp(i\omega_{ext}t)\hat{D}_H(0) \tag{2.4.14}$$

$$\hat{D}_H(t) = \left[\left(\Delta_\omega\Omega_{ext}/2\Omega_\Delta^2\right)(\cos(2\Omega_\Delta t) - 1) + (i\Omega_{ext}/\Omega_\Delta)\sin(2\Omega_\Delta t)\right]\hat{\sigma}_H(0) + \left[\left(\Delta_\omega\Omega_{ext}/2\Omega_\Delta^2\right)(\cos(2\Omega_\Delta t) - 1) - (i\Omega_{ext}/\Omega_\Delta)\sin(2\Omega_\Delta t)\right]\hat{\sigma}_H^\dagger(0) + \left[\left(\Delta_\omega^2/4\Omega_\Delta^2\right) + \left(\Omega_{ext}^2/\Omega_\Delta^2\right)\cos(\Omega_\Delta t)\right]\hat{D}_H(0) \tag{2.4.15}$$

Now, we have to find the expectation values of these operators. Since, in the Heisenberg picture, the time evolution of a system is described by time-dependent operators while the wave functions are time-independent, the expectation value of an operator can be found by averaging over the initial wave function (see Eq. (2.1.5)). Assuming that at the initial moment, the system is in the ground state

$$|\Psi_H\rangle = |\Psi_{Schr}(0)\rangle = |g\rangle$$

we obtain $\langle\hat{\sigma}_H(0)\rangle = \left\langle\hat{\sigma}_H^\dagger(0)\right\rangle = 0$ and $\left\langle\hat{D}_H(0)\right\rangle = -1$. Then,

$$\langle\hat{\sigma}_H(t)\rangle = -\left[\left(\Delta_\omega\Omega_{ext}/4\Omega_\Delta^2\right)(\cos(2\Omega_\Delta t) - 1) + (i\Omega_{ext}/2\Omega_\Delta)\sin(2\Omega_\Delta t)\right]\exp(-i\omega_{ext}t) \tag{2.4.16}$$

$$\left\langle\hat{\sigma}_H^\dagger(t)\right\rangle = -\left[\left(\Delta_\omega\Omega_{ext}/4\Omega_\Delta^2\right)(\cos(2\Omega_\Delta t) - 1) - (i\Omega_{ext}/2\Omega_\Delta)\sin(2\Omega_\Delta t)\right]\exp(i\omega_{ext}t) \tag{2.4.17}$$

$$\left\langle\hat{D}_H(t)\right\rangle = -\left[\left(\Delta_\omega^2/4\Omega_\Delta^2\right) + \left(\Omega_{ext}^2/\Omega_\Delta^2\right)\cos(2\Omega_\Delta t)\right] \tag{2.4.18}$$

Equations (2.4.16)–(2.4.18) show that the solutions for the expectation values of the operators $\hat{\sigma}_H(t)$, $\hat{\sigma}_H^\dagger(t)$, and $\hat{D}_H(t)$ have no stationary states. The time evolution of a TLS placed in the external classical field is reduced to the driven oscillation on the frequency of the external field, which is modulated with the frequency $2\Omega_{ext}$. These solutions describe the *Rabi oscillations* of the population inversion with the frequency $2\Omega_\Delta$.

The response of the system to the external field is nonlinear. This is manifested, first, in the nonlinear dependence of the response amplitude $\hat{\sigma}(t)$ on the external field amplitude (recall that $\Omega_\Delta = \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}/2$ is a function of Ω_{ext} and $\Omega_{ext} = -d_{eg}E/(2\hbar)$). Also, $\hat{\sigma}(t)$, which is proportional to the dipole moment of the TLS, oscillates not only with the frequency of the external field ω_{ext} but also with the side frequencies $\omega_{ext} \pm 2\Omega_\Delta$. Note that in the case of the resonance, $\Delta = 0$, the population inversion oscillates between -1 and 1 with the frequency $2\Omega_{ext}$:

$$\left\langle \hat{D}_H(t) \right\rangle = -\cos(2\Omega_{ext}t), \tag{2.4.19}$$

while the driven oscillation of the dipole moment occurs on the carrying frequency ω_{ext} and is modulated with the frequency $2\Omega_{ext}$:

$$\langle \hat{\sigma}_H(t) \rangle = -(i/2)\sin(2\Omega_{ext}t)\exp(-i\omega_{ext}t) \tag{2.4.20}$$

It is worth emphasizing that the problem of the atom interaction with a single EM mode is considered by using the Hermitian Hamiltonian while radiation losses are disregarded. The radiation processes in this formulation cannot be considered because this would require expanding the system by adding the reservoir of emitted photons, which does not belong to the primary Hermitian system. Therefore, as a result, we obtained only the periodic time evolution of the Hermitian system.

To conclude, in a closed system of a single incident mode of the classical EM field and an atom, neither an excitation of an atom due to the absorption of a photon nor its relaxation with photon emission can be described correctly. In other words, a single mode of an external field cannot cause atomic transitions from one stationary state to another, as studied in spectroscopy. The spectroscopy approach implies a hidden assumption about the system's interaction with a reservoir of emitted photons. In particular, the concept of the stationary state lifetime can be introduced phenomenologically.

2.5 The Interaction of a Two-Level System with a Single Mode of Quantized Field (The Jaynes-Cummings Approach)

2.5.1 Quantization of Electromagnetic Fields

In the previous section, we discussed a TLS interaction with a single mode of a classical EM field. According to Planck's theory, the radiation energy should be quantized; after the quantization, the problem becomes more complicated. However, the main conclusion does not change: the TLS and the incident field evolve periodically, forming a unified Hermitian system [2, 14, 15].

Let us sketch the quantization procedure for the EM mode. Using the identity

$$\nabla \times (\nabla \times \mathbf{v}) = \nabla(\nabla \cdot \mathbf{v}) - \nabla^2 \mathbf{v}, \tag{2.5.1}$$

Maxwell's equations, in vacuum

$$\nabla \times \mathbf{E} = -(1/c)\partial \mathbf{B}/\partial t, \tag{2.5.2}$$

$$\nabla \times \mathbf{B} = (1/c)\partial \mathbf{E}/\partial t, \tag{2.5.3}$$

$$\nabla \cdot \mathbf{E} = 0, \nabla \cdot \mathbf{B} = 0 \tag{2.5.4}$$

can be reduced to the wave equations

$$\nabla^2 \mathbf{E} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{E} = 0 \tag{2.5.5}$$

It is convenient to search for the solution to these equations by presenting the electric fields as a sum:

$$\mathbf{E}(t, \mathbf{r}) = \frac{1}{2}\sum\nolimits_{\mathbf{m}} \left(E_{\mathbf{m}}(t)\mathbf{u}_{\mathbf{m}}(\mathbf{r}) + E^*_m(t)\mathbf{u}^*_m(\mathbf{r})\right), \tag{2.5.6}$$

where the complex mode function $\mathbf{u}_{\mathbf{m}}$ is an eigenfunction of the problem

$$\begin{gathered} \nabla^2 \mathbf{u}_{\mathbf{m}} + (\mathbf{k}_{\mathbf{m}} \cdot \mathbf{k}_{\mathbf{m}})\mathbf{u}_{\mathbf{m}} = 0, \\ \nabla \cdot \mathbf{u}_{\mathbf{m}} = 0, \\ \mathbf{u}_{\mathbf{m}}(r_i + L) = \mathbf{u}_{\mathbf{m}}(r_i) \end{gathered} \tag{2.5.7}$$

where the last equation is a periodic condition for functions $\mathbf{u}_{\mathbf{m}}(\mathbf{r})$. The length L is the size of the quantization box.

Conditions (2.5.7) correspond to a Hermitian problem. Hence, the set of eigenfunctions $\mathbf{u}_m$ is complete, and they can be made orthogonal with respect to the scalar product:

$$\int_V \mathbf{u}_{\mathbf{m}'} \cdot \mathbf{u}^*{}_{\mathbf{m}} dV = V\delta_{\mathbf{m}\mathbf{m}'}. \tag{2.5.8}$$

Substituting series (2.5.6) into Eq. (2.5.5) and employing Eq. (2.5.8), we can show that each mode amplitude $E_{\mathbf{m}}(t)$ satisfies the following equations:

$$(\mathbf{k}_{\mathbf{m}} \cdot \mathbf{k}_{\mathbf{m}})E_{\mathbf{m}}(t) + \frac{1}{c^2}\frac{d^2}{dt^2}E_{\mathbf{m}}(t) = 0. \tag{2.5.9}$$

Thus, the amplitudes $E_{\mathbf{m}}(t)$ are solutions to the equation for a harmonic oscillator with the frequency:

$$\omega_{\mathbf{m}} = c\sqrt{(\mathbf{k}_{\mathbf{m}} \cdot \mathbf{k}_{\mathbf{m}})}. \tag{2.5.10}$$

Equation (2.5.7) imposes the following restrictions on the values of $\mathbf{k}_{\mathbf{m}}$:

$$\begin{aligned} k_{\mathbf{m}x}L &= 2\pi n_x, \\ k_{\mathbf{m}y}L &= 2\pi n_y, \\ k_{\mathbf{m}z}L &= 2\pi n_z. \end{aligned} \tag{2.5.11}$$

Here n_x, n_y, and n_z are integers satisfying condition (2.5.10). In the $\mathbf{k}$-space, the allowed values of the wave vectors form a grid with the spacing of $(2\pi/L)$, and each $\mathbf{k}$-state occupies the volume $(2\pi/L)^3$. At the end of the calculations, we have to take the limit $L \to \infty$, after which the vector $\mathbf{k}_{\mathbf{m}}$ can point in any direction.

Similarly, for magnetic induction $\mathbf{B}$, we can obtain:

$$\mathbf{B} = \sum\nolimits_{\mathbf{m}} k_m^{-1} B_{\mathbf{m}}(t)\mathbf{w}_{\mathbf{m}}, \tag{2.5.12}$$

where $\mathbf{w}_{\mathbf{m}}$ satisfies Eq. (2.5.7). To determine $\mathbf{w}_{\mathbf{m}}$, we substitute Eqs. (2.5.6) and (2.5.12) into Eq. (2.5.2) to obtain

$$\sum\nolimits_{\mathbf{m}} E_{\mathbf{m}}(t) \nabla \times \mathbf{u}_{\mathbf{m}}(\mathbf{r}) = -(1/c) \sum\nolimits_{\mathbf{m}} \frac{\partial}{\partial e} B_{\mathbf{m}}(t)\mathbf{w}_{\mathbf{m}}.$$

Thus, we can use $\mathbf{w}_{\mathbf{m}} = (k_m)^{-1} \nabla \times \mathbf{u}_{\mathbf{m}}$, because these functions satisfy Eq. (2.5.7). The orthogonality of $\nabla \times \mathbf{u}_{\mathbf{m}}$ allows us to obtain the following equation:

$$E_{\mathbf{m}}(t) \nabla \times \mathbf{u}_{\mathbf{m}}(\mathbf{r}) = -(1/c) \frac{\partial}{\partial t} B_{\mathbf{m}}(t) \nabla \times \mathbf{u}_{\mathbf{m}}(\mathbf{r}),$$

or

$$E_{\mathbf{m}}(t) = -\left(\frac{1}{ck_m}\right) \frac{\partial}{\partial t} B_{\mathbf{m}}(t) = i \frac{\omega_m}{ck_m} B_{\mathbf{m}}(t) = iB_{\mathbf{m}}(t) \tag{2.5.13}$$

If eigenfunctions $\mathbf{u}_m$ are chosen to be complex, then for real fields $\mathbf{E}$, the amplitudes $E_m(t)$ and $B_m(t)$ should also be complex, and we can write:

$$\mathbf{E} = \sum_{m=-\infty}^{\infty} E_m \mathbf{u}_m = \sum_{m=-\infty}^{\infty} E_m^* \mathbf{u}_m^* = \frac{1}{2}\left(\sum_{m=-\infty}^{\infty} E_m \mathbf{u}_m + \sum_{m=-\infty}^{\infty} E_m^* \mathbf{u}_m^*\right) \tag{2.5.14}$$

$$\mathbf{B} = \frac{1}{2}\sum\nolimits_m k_m^{-1}\left(B_m(t)\nabla\times\mathbf{u}_m + B_m^*(t)\nabla\times\mathbf{u}_m^*\right) \tag{2.5.15}$$

Then, the energy density of the electric field takes the form:

$$\frac{1}{8\pi}\mathbf{E}_{re}^2 = \frac{1}{32\pi}\left(\sum_{m=-\infty}^{\infty} E_m\mathbf{u}_m + \sum_{m'=-\infty}^{\infty} E_{m'}^*\mathbf{u}_{m'}^*\right)$$
$$\left(\sum_{m''=-\infty}^{\infty} E_{m''}\mathbf{u}_{m''} + \sum_{m'''=-\infty}^{\infty} E_{m'''}^*\mathbf{u}_{m'''}^*\right) = \frac{1}{16\pi}\sum_{m,\,m'=-\infty}^{\infty} E_{m'}^* E_m\mathbf{u}_{m'}^*\mathbf{u}_m$$

Here, we neglect the terms oscillating at a double frequency because they cancel each other when the energy of the magnetic field is added.

In the same way, we obtain the energy density of the magnetic field:

$$\frac{1}{8\pi}\mathbf{B}_{re}^2 = \frac{1}{16\pi}\sum_{m,\,m'} k_m^{-1}k_{m'}^{-1}B_{m'}^*B_{m''}\left(\nabla\times\mathbf{u}_m\right)\left(\nabla\times\mathbf{u}_{m'}^*\right)$$

The Hamiltonian for the EM fields can be represented as

$$\begin{aligned} H &= \frac{1}{8\pi}\int_V \left(E^2(t,z) + B^2(t,z)\right)dV \\ &= \frac{1}{16\pi}\sum\nolimits_{m'm} E_{m'}E_m^*\int_V \mathbf{u}_{m'}\mathbf{u}_m^* dV + \frac{1}{16\pi}\sum\nolimits_{m'm} B_{m'}B_m^*\int_V k_m^{-1}\nabla\times\mathbf{u}_m k_{m'}^{-1}\nabla\times\mathbf{u}_m^* dV \\ &= \frac{V}{16\pi}\sum\nolimits_m \left(E_mE_m^* + B_mB_m^*\right) = \frac{V}{8\pi}\sum\nolimits_m E_mE_m^* = \sum\nolimits_m H_m \end{aligned} \tag{2.5.16}$$

where we use the equality $E_mE_m^* = B_mB_m^*$, which comes from equalities $E_m(t) = iB_m(t)$ and $E_m^*(t) = -iB_m^*(t)$ (see Eq. (2.5.13)). Finally, we arrive at the following Hamiltonian of the m-th mode:

$$H_m = \frac{V}{8\pi}E_mE_m^* = \frac{V}{16\pi}\left(E_m^*E_m + E_mE_m^*\right) \tag{2.5.17}$$

In quantum mechanics, we should introduce the Hermitian operators corresponding to each physical quantity. For these operators, complex conjugation is replaced by Hermitian conjugation.

Note that the quantities $E_m(t)$ and $E_m^*(t)$ cannot be related with Hermitian operators because complex conjugations do not transform these quantities into themselves. For example, by associating $E_m(t)$ and $E_m^*(t)$ with operators $\hat{E}_m(t)$ and $\hat{E}_m^\dagger(t)$, we obtain that the Hermitian conjugation transforms them into each other but not into themselves.

Usually, the field quantization is performed by analogy with the quantization procedure for a quantum oscillator. To bring Hamiltonian (2.5.17) to a form convenient for quantization, we transition from quantities $\hat{E}_m(t)$ and $\hat{E}_m^\dagger(t)$ to new operators, in which Hamiltonian (2.5.17) takes the form of the Hamiltonian of a quantum oscillator. Namely, we introduce quadrature operators, which are Hermitian:

$$\omega_m \hat{Q}_m = \left(\hat{E}_m + \hat{E}_m^\dagger\right)\sqrt{V/16\pi}, \hat{P}_m = -i\left(\hat{E}_m - \hat{E}_m^\dagger\right)\sqrt{V/16\pi} \tag{2.5.18}$$

Taking into account that

$$\hat{E}_m = \left(\omega_m \hat{Q}_m + i\hat{P}_m\right)/\sqrt{V/4\pi}, \hat{E}_m^\dagger = \left(\omega_m \hat{Q}_m - i\hat{P}_m\right)/\sqrt{V/4\pi} \tag{2.5.19}$$

we map the EM mode problem to the harmonic oscillator problem because Hamiltonian (2.5.17) becomes the Hamiltonian of oscillator with unit mass:

$$\begin{aligned}\frac{V}{16\pi}\left(\hat{E}_m\hat{E}_m^\dagger + \hat{E}_m^\dagger\hat{E}_m\right) &= \frac{V}{16\pi}\Big[\left(\omega_m\hat{Q}_m + i\hat{P}_m\right)\left(\omega_m\hat{Q}_m - i\hat{P}_m\right) \\ &\quad + \left(\omega_m\hat{Q}_m - i\hat{P}_m\right)\left(\omega_m\hat{Q}_m + i\hat{P}_m\right)\Big]/(V/4\pi) \\ &= \left(\omega_m^2\hat{Q}_m^2/2 + \hat{P}_m^2/2\right)\end{aligned} \tag{2.5.20}$$

where $\hat{Q}_m$ and $\hat{P}_m$ play the roles of the coordinate and the momentum operators for the oscillator, respectively.

In accordance with the quantization method [3] (see also Remark 2.2), operators $\hat{Q}_m$ and $\hat{P}_m$ should have the commutation relation:

$$\left[\hat{Q}_m, \hat{P}_m\right] = i\hbar \tag{2.5.21}$$

For the quantum harmonic oscillator, we can introduce the creation $\hat{a}^\dagger$ and annihilation $\hat{a}$ operators:

$$\hat{a}_m = \frac{\left(\omega_m\hat{Q}_m + i\hat{P}_m\right)}{\sqrt{2\omega_m\hbar}}, \hat{a}_m^\dagger(t) = \frac{\left(\omega_m\hat{Q}_m - i\hat{P}_m\right)}{\sqrt{2\omega_m\hbar}} \tag{2.5.22}$$

having the commutator $[a, a^\dagger] = 1$ (see Problem 1.4).

Finally, we can introduce the field operators:

$$\hat{E}_m = \sqrt{8\pi\hbar\omega_m/V}\hat{a}_m, \quad \hat{E}_m^\dagger = \sqrt{8\pi\hbar\omega_m/V}\hat{a}_m^\dagger \tag{2.5.23}$$

to present the Hermitian field operators of real electric and magnetic fields as the Fourier sum over the creation $\hat{a}^{\dagger}$ and annihilation $\hat{a}$ operators:

$$\hat{\mathbf{E}} = \sum\nolimits_m \sqrt{\frac{2\pi\hbar\omega_m}{V}}\left(\mathbf{u}_m\hat{a}_m + \mathbf{u}_m^*\hat{a}_m^{\dagger}\right), \mathbf{B}_{re} = i\sum\nolimits_m \sqrt{\frac{2\pi\hbar\omega_m}{V}}k_m^{-1}\left(\hat{a}_m^{\dagger}\nabla\times\mathbf{u}_m - \hat{a}_m\nabla\times\mathbf{u}_m^*\right). \tag{2.5.24}$$

Note that $\hat{E}_m$ and $\hat{E}_m^{\dagger}$ play the role of annihilation and creation operators for excitations of $\mathbf{u}_m$ mode, and the value

$$E_{m0} = \sqrt{2\pi\hbar\omega_m/V} \tag{2.5.25}$$

has the meaning of the electric field per one photon with frequency ω_m.

The eigenfrequencies of the Hamiltonian

$$\hat{H}_m = \omega_m^2\hat{Q}_m^2/2 + \hat{P}_m^2/2 \tag{2.5.26}$$

are $\omega_{mn} = \omega_m(n + 1/2)$, $n = 0, 1, 2, \ldots$ with corresponding eigenstates $|n\rangle$, which are called Fock states [12] (see Problem 1.4). The number n, which determines the energy of the eigenstate, is interpreted as a number of quanta $\hbar\omega_a$ contained in the eigenstate $|n\rangle$.

The operator $\hat{a}$ acting on the state with n quanta, $|n\rangle$, transitions this state to the state $|n - 1\rangle$ with $n - 1$ quanta; for this reason, it is called the annihilation (or lowering) operator; the operator $\hat{a}^{\dagger}$ moves the state $|n\rangle$ with n quanta to the state $|n + 1\rangle$ with $n + 1$ quanta and is called the creation (or rising) operator. Mathematically, this can be represented as (Problem 1.4):

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle \text{ and } \hat{a}^{+}|n\rangle = \sqrt{n+1}|n+1\rangle$$

The zero level of energy can be set arbitrarily. This is because for any operator $\hat{A}$, the Heisenberg equation of motion is determined by the commutator of the operator with the Hamiltonian. The commutator is not changed if we add a constant to the Hamiltonian (the identity operator $\hat{I}$ commutes with any operator). For future consideration, we subtract $\hat{I}\hbar\omega_a/2$ from $\hat{H} = \hbar\omega_a\left(\hat{a}^{\dagger}\hat{a} + \hat{I}/2\right)$ turning it into the Hamiltonian becomes $\hat{H} = \hbar\omega_a\hat{a}^{\dagger}\hat{a}$. The ground state of the harmonic oscillator corresponding to the latter Hamiltonian has zero energy.

2.5.2 *Eigenfunctions of the Jaynes-Cummings Problem*

In Sect. 2.4 we have considered the Rabi oscillation of excitations of an atom placed in a classical monochromatic field. Since the classical plane wave has infinite energy, it is impossible to correctly describe the energy exchange between the atom and the

field. Therefore, in this section, we consider the behavior of an atom placed in the field of a quantized mode.

As before, we model an atom interacting with a quantized external field by the TLS with the transition frequency ω_σ. Thus, the TLS Hamiltonian, $\hat{H}_{TLS}$, is equal to $\hbar\omega_\sigma\hat{\sigma}^\dagger\hat{\sigma}$ (see Eq. (2.2.11)). We focus on the problem in which the TLS is placed in a resonator, and only one resonator mode is in resonance with the atomic transition while other modes are off-resonant. Thus, we confine ourselves to considering only one resonator mode, which has the frequency ω_a. The Hamiltonian of the resonant mode, which we consider as a quantum oscillator, is

$$\hat{H}_E = \hbar\omega_a\hat{a}^\dagger\hat{a} \tag{2.5.27}$$

The Hamiltonian of the interaction between the TLS and the mode is written in the dipole approximation $\hat{H}_{\text{int}} = -\hat{\mathbf{d}}\cdot\hat{\mathbf{E}}$. As in the previous section, the operator of the dipole moment can be expressed via the transition operators between ground and excited states, $\hat{\mathbf{d}} = \mathbf{d}_{eg}\left(\hat{\sigma}^\dagger + \hat{\sigma}\right)$. The operator of the electric field mode $\hat{\mathbf{E}}$ can be expressed as $\hat{\mathbf{E}} = \mathbf{E}_0\left(\hat{a}^\dagger + \hat{a}\right)$, where $\mathbf{E}_0$ is the electric field "per one photon" (see Eq. (2.5.25) and Remark 2.4). In what follows, we assume that the atom is isotropic and that the induced dipole moment is parallel to the external field. This allows us to transition from vectors to scalars, $\mathbf{d}_{eg}\cdot\mathbf{E}_0 = d_{eg}E_0$. Thus, the interaction Hamiltonian has the form:

$$\hat{H}_{int} = -\hat{\mathbf{d}}\cdot\hat{\mathbf{E}} = \hbar\Omega_a\left(\hat{a}+\hat{a}^\dagger\right)\left(\hat{\sigma}+\hat{\sigma}^\dagger\right) \tag{2.5.28}$$

with $\Omega_a = -d_{eg}\sqrt{2\pi\omega_a/V\hbar}$. Using the rotating wave approximation (see Eq. (2.4.12)), we arrive at the Jaynes-Cummings Hamiltonian:

$$\hat{H}_{JC} = \hbar\omega_a\hat{a}^\dagger\hat{a} + \hbar\omega_\sigma\hat{\sigma}^\dagger\hat{\sigma} + \hbar\Omega_a\left(\hat{\sigma}^\dagger\hat{a} + \hat{\sigma}\hat{a}^\dagger\right). \tag{2.5.29}$$

Note that for quantized fields, the constant Ω_a plays the role of the interaction constant of the atom (TLS) with the mode characterized by the frequency ω_a.

In the absence of the interaction ($\Omega_a = 0$), eigenstates of Hamiltonian (2.5.29) are the direct products of the eigenstates of an isolated atom and a mode containing n photons $|g,n\rangle \equiv |g\rangle|n\rangle$ and $|e,n\rangle \equiv |e\rangle|n\rangle$, $n = 0, 1, 2, \ldots$. The eigenvalues corresponding to these eigenstates are the sums of eigenvalues of the Hamiltonian of the isolated atom and the Hamiltonian of the mode, i.e., $n\hbar\omega_a$ for the state $|g,n\rangle$ and $\hbar\omega_\sigma + n\hbar\omega_a$ for the state $|e,n\rangle$. Moreover, these eigenstates are also eigenstates of the operator of the total number of excitations in the system, $\hat{N} = \hat{a}^\dagger\hat{a} + \hat{\sigma}^\dagger\hat{\sigma}$, namely, $\hat{N}|g,n\rangle = \left(\hat{a}^\dagger\hat{a} + \hat{\sigma}^\dagger\hat{\sigma}\right)|g,n\rangle = n|g,n\rangle$ and $\hat{N}|e,n\rangle = \left(\hat{a}^\dagger\hat{a} + \hat{\sigma}^\dagger\hat{\sigma}\right)|e,n\rangle = (n+1)|e,n\rangle$. The linear combinations of the normalized wave functions $|g,n\rangle$ and $|e,n\rangle$ form the two-dimensional Hilbert space of the Jaynes-Cummings Hamiltonian.

Jaynes-Cummings Hamiltonian (2.5.29) commute with the operator $\hat{N} = \hat{a}^\dagger \hat{a} + \hat{\sigma}^\dagger \hat{\sigma}$ (see Problem 1.5). It means that these operators share the eigenstates. Although the states $|e, n\rangle \equiv |e\rangle|n\rangle$ and $|g, n\rangle \equiv |g\rangle|n\rangle$ are eigenstates of the operator $\hat{N} = \hat{a}^\dagger \hat{a} + \hat{\sigma}^\dagger \hat{\sigma}$, these are not eigenstates of the interaction operator $\hbar\Omega_a\left(\hat{\sigma}^\dagger \hat{a} + \hat{\sigma}\hat{a}^\dagger\right)$ and, consequently, of the Jaynes-Cummings Hamiltonian. Below, we find the true eigenstates.

The structure of the interaction operator prompts us that the states $|e, n\rangle \equiv |e\rangle|n-1\rangle$ and $|g, n\rangle \equiv |g\rangle|n\rangle$ have the same number of excitations. Moreover, the interaction Hamiltonian transforms the $|e, n-1\rangle$ state into the $|g, n\rangle$ state:

$$\hbar\Omega_a\left(\hat{\sigma}^\dagger \hat{a} + \hat{\sigma}\hat{a}^\dagger\right)|e, n-1\rangle = \hbar\Omega_a\sqrt{n}|g, n\rangle \tag{2.5.30}$$

and vice versa—the $|e, n-1\rangle$ state into the $|g, n\rangle$ state

$$\hbar\Omega_a\left(\hat{\sigma}^\dagger \hat{a} + \hat{\sigma}\hat{a}^\dagger\right)|g, n\rangle = \hbar\Omega_a\sqrt{n}|e, n-1\rangle \tag{2.5.31}$$

Thus, under the action of the interaction operator, the number of photons in the mode increases or decreases by one, respectively, while the number of the atom excitations changes in the opposite way. Thus, although the interaction Hamiltonian changes the number of excitations in the atomic and/or photon subsystems, the total number of excitations is conserved.

For fixed n, the normalized linear combinations of the vectors $|e, n-1\rangle$ and $|g, n\rangle$ determine the two-dimensional Hilbert subspace spanned on these vectors. Thus, the Hilbert space of the wave functions of Hamiltonian (2.5.29) becomes the sum of such subspaces. The matrices of both the Jaynes-Cummings Hamiltonian and the operator $\hat{N} = \hat{a}^\dagger \hat{a} + \hat{\sigma}^\dagger \hat{\sigma}$ become block-diagonal. In particular, in the basis $\{|e, n-1\rangle, |g, n\rangle\}$, the $(n-1)$-*th* block Hamiltonian can be written as

$$\hat{H}^{(n-1)} = \begin{pmatrix} (n-1)\hbar\omega_a + \hbar\omega_\sigma & \hbar\Omega_a\sqrt{n} \\ \hbar\Omega_a\sqrt{n} & n\hbar\omega_a \end{pmatrix}. \tag{2.5.32}$$

Here, we used Eqs. (2.5.30) and (2.5.31) and that the basis belongs to the eigenstates of the Hamiltonian of an isolated atom.

The eigenfrequencies of the eigenstates ($|+, n\rangle$ and $|-, n\rangle$) of the Hamiltonian $\hat{H}^{(n-1)}$ can be written as

$$\omega_{\pm,n} = (n-1)\omega_a + (\omega_a + \omega_\sigma)/2 \pm \sqrt{\Omega_a^2 n + (\Delta_a/2)^2}, n = 1, 2, \ldots \tag{2.5.33}$$

where $\Delta_a = \omega_a - \omega_\sigma$. The eigenfunctions of this Hamiltonian can be written as

$$\begin{aligned} |+, n\rangle &= \cos\varphi_n|e, n-1\rangle + \sin\varphi_n|g, n\rangle, \\ |-, n\rangle &= -\sin\varphi_n|e, n-1\rangle + \cos\varphi_n|g, n\rangle, n = 1, 2, \ldots; \end{aligned} \tag{2.5.34}$$

and

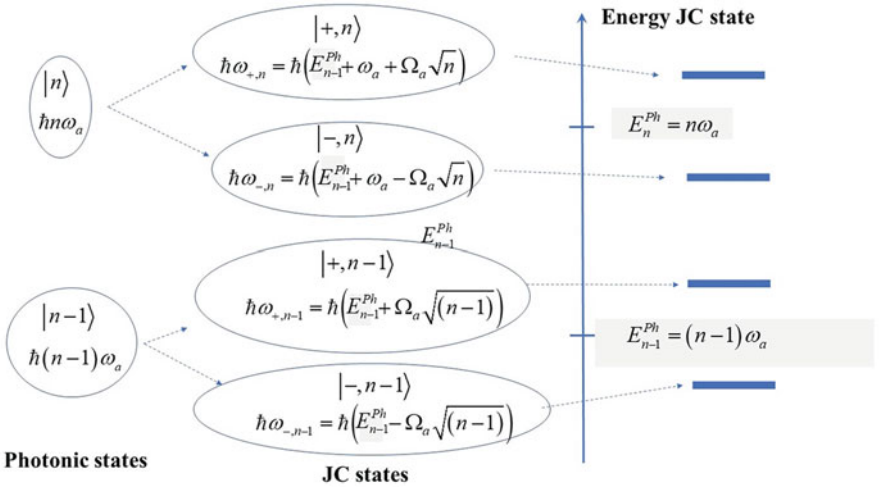

Fig. 2.1 The scheme of the energy levels of the Jaynes-Cummings system for the resonant case $\Delta_a = 0$ and $\Omega_a\sqrt{n} < \omega_a$

$$\begin{aligned} |g,n\rangle &= \sin\varphi_n|+,n\rangle + \cos\varphi_n|-,n\rangle \\ |e,n-1\rangle &= \cos\varphi_n|+,n\rangle - \sin\varphi_n|-,n\rangle \end{aligned} \tag{2.5.35}$$

where $\tan(2\varphi_n) = -2\Omega_a\sqrt{n}/\Delta_a$ (see Problem 1.5). The energy difference between the states $|+,n\rangle$ and $|-,n\rangle$ is equal to $2\hbar\sqrt{\Omega_a^2 n + (\Delta_a/2)^2}$.

In addition to states (2.5.34), there is the ground state that does not have photons ($n = \langle\hat{a}^\dagger\hat{a}\rangle = 0$):

$$|g,0\rangle. \tag{2.5.36}$$

We assume that the energy of this state is zero.

If $\Omega_a\sqrt{n} \gg \Delta_a/2$, we are close to the resonance ($\Delta_a = 0$), and the energies of eigenstates form the same pairs $\{\hbar\omega_{+,n}, \hbar\omega_{-,n}\}$, which are separated by $\hbar\omega_a$. Inside each pair, the separation is $\hbar\Omega_a\sqrt{n}$. So that when $\Omega_a\sqrt{n} < \omega_a$, the energy of the state $|-,n\rangle$ is lower than the energy of the state $|+,n-1\rangle$ (see Fig. 2.1).

In the book, we mainly deal with the off-resonance cases with a large frequency difference $\Delta_a/2 \gg \Omega_a$. For the small number of photons $\sqrt{n} \ll \Delta_a/(2\Omega_a)$, from Eq. (2.5.33), we obtain:

$$\begin{aligned} \omega_{+,n} &\simeq (n-1)\omega_a + (\omega_\sigma+\omega_a)/2 + (\omega_\sigma-\omega_a)/2 \\ &= n\omega_a - \omega_a + (\omega_\sigma+\omega_a+\omega_\sigma-\omega_a)/2 = \omega_\sigma - \omega_a + n\omega_a = n\omega_a + |\Delta_a|, \\ \omega_{-,n} &\simeq (n-1)\omega_a + (\omega_\sigma+\omega_a)/2 - (\omega_\sigma-\omega_a)/2 \\ &= n\omega_a - \omega_a + (\omega_\sigma+\omega_a-\omega_\sigma+\omega_a)/2 = n\omega_a. \end{aligned} \tag{2.5.37}$$

According to these equations, the energies form the equidistant pairs $\{\hbar\omega_{+,\,n}, \hbar\omega_{-,\,n}\}$, with the energy difference between the states inside the pair equals to $\hbar\Delta_a = \hbar\omega_\sigma - \hbar\omega_a$, while the energy difference between pairs ($\hbar\omega_{+,\,n} - \hbar\omega_{+,\,n\,-\,1} = \hbar\omega_{-,\,n} - \hbar\omega_{-,\,n\,-\,1}$) is equal to $\hbar\omega_a$. Thus, if $\hbar\omega_a > \hbar\omega_\sigma - \hbar\omega_a$, the energy $\hbar\omega_{-,\,n}$ is higher than the energy $\hbar\omega_{+,\,n\,-\,1}$.

To conclude, since Jaynes-Cummings states (2.5.34) and (2.5.36) are the system eigenstates, if, initially, the system was in one of these states, it would remain in the same state. Thus, the Jaynes-Cummings description of an atom interacting with a single-mode quantum EM field confirms the conclusion of the previous section that in such a closed system, electronic transitions between the Jaynes-Cummings eigenstates cannot occur.

2.6 The Bloch Vector Formalism Based on Floquet's Theorem

In the previous section, we have found the eigenstates of the time-dependent Hamiltonian in which the interaction term depends on time harmonically. Now, we consider a general approach to this problem.

To describe the evolution of a system whose Hamiltonian depends on time periodically, the Bloch vector formalism has been developed in Refs. [10, 14, 16, 17]. This approach is based on Floquet's theorem [18] (see Remark 2.5 for detail); it is analogous to the approach used in solid-state crystals, in which Bloch vectors describe the motion of electrons in a periodic lattice. In this section, we illustrate this formalism by considering the Rabi oscillations of a TLS. In this simple case, Bloch and Rabi frequencies coincide.

Remark 2.5 **Floquet's theorem**. According to Floquet's theorem, for a system of M equations $d\mathbf{x}/dt = \mathbf{A}(t)\mathbf{x}$, where $\mathbf{A}(t)$ is an $M \times N$ matrix that depends on time periodically with the period T, a general solution can be expanded over the full set of N Floquet's functions $\{\exp\left(-i\omega_F^\alpha t\right)|\mathbf{\Phi}_\alpha(t)\rangle\}$, where ω_F^α ($\alpha = 1, \ldots, N$) do not depend on time. These quantities are called quasi-energies (or quasi-frequencies, or Floquet's frequencies); the state vectors $|\mathbf{\Phi}_\alpha(t)\rangle = |\mathbf{\Phi}_\alpha(t + T)\rangle$ periodically depend on time.

Let us describe a TLS by the unperturbed Hamiltonian $\hat{H}_{TLS}$ (Eq. (2.2.11)). We assume that time-dependent Schrödinger wave functions of excited and ground states $|\psi_k^{Schr}\rangle = \exp(-iE_k t/\hbar)|\psi_k\rangle$ are known (here, $|\psi_1\rangle = |g\rangle$ and $|\psi_2\rangle = |e\rangle$ are wave functions of ground and excited states, respectively). Since $\hat{H}_{TLS}$ is time-independent, its eigenfunctions also do not depend on time. Thus,

$$\hat{H}_{TLS}|\psi_k\rangle = E_k|\psi_k\rangle. \tag{2.6.1}$$

We assume that the TLS is under the periodic perturbation $\hat{V}(t) = \hat{V}(t+T)$ of a classical EM field. In particular, this perturbation may be harmonic with the period T and the frequency $\omega_{ext} = 2\pi/T$. Then, the Hamiltonian of the system is

$$\hat{H}_{dTLS} = \hat{H}_{TLS} + \hat{V}(t).$$

We also assume that $\hat{V}(t)$ is defined by external conditions that are not affected by the system states.

We expand the wave function $|\psi(t)\rangle$ of the Hamiltonian $\hat{H}_{dTLS}$ over the basis $|\psi_k\rangle$ of the eigenfunctions of the Hamiltonian $\hat{H}_{TLS}$:

$$|\psi(t)\rangle = \sum_{k=1}^{2} c_k(t)|\psi_k\rangle, \tag{2.6.2}$$

where the subscript $k = 1$ corresponds to the ground state $|g\rangle$ and $k = 2$ corresponds to the excited state $|e\rangle$.

Now, let us substitute expansion (2.6.2) into the Schrödinger equation and scalar multiply the obtained equation by $\langle\psi_k|$. As a result, we obtain a system of two linear differential equations for the functions $c_k(t)$:

$$i\hbar\frac{dc_k(t)}{dt} = c_k(t)E_k + \sum_{l=1}^{2} V_{kl}(t)c_l(t), \qquad (k=1,2) \tag{2.6.3}$$

where $V_{kl}\langle\psi_k|\hat{V}|\psi_l\rangle$. The coefficients of this system periodically depend on time. According to Floquet's theorem, the solution of this system is a superposition of Floquet's functions that can be represented as

$$\mathbf{c}_F(t) = \mathbf{f}(t)\exp(-i\omega_F t), \tag{2.6.4}$$

where

$$\mathbf{c}_F(t) = \begin{bmatrix} c_1(t) \\ c_2(t) \end{bmatrix},$$

and

$$\mathbf{f}(t) = \begin{bmatrix} f_1(t) \\ f_2(t) \end{bmatrix} = \mathbf{f}(t+T)$$

is a vector function that depends on time with the same period as the operator $\hat{V}(t)$; ω_F is yet unknown frequency, called Floquet's frequency. As it follows from the general theory [19], ω_F is defined with the accuracy up to an additive $n\omega_{\text{ext}}$, which does not affect $\mathbf{c}_F(t)$ but replaces the periodic part $\mathbf{f}(t)$ with $\mathbf{f}(t)\exp(in\omega_{ext}t)$. In other words, the frequencies $\omega_F + n\omega_{\text{ext}}$ and ω_F correspond to the same Floquet's function. When the atom is modeled by a TLS, the number of Floquet's frequencies is two.

For what follows, it is convenient to employ the Fourier series of the periodic functions $f_k(t)$ and $\hat{V}(t)$:

$$f_k(t) = \sum_{n=0}^{N} f_k^{(n)} \exp(-i\omega_{ext}nt), \tag{2.6.5}$$

$$V_{kl}(t) = V_{kl}^{(1)} \exp(-i\omega_{ext}t) + V_{kl}^{(-1)} \exp(i\omega_{ext}t), \tag{2.6.6}$$

where N can be infinite [10]. Substituting these Fourier series into Eq. (2.6.3), we obtain a system of algebraic equations for the Fourier coefficients $f_k^{(n)}$:

$$\begin{aligned}\hbar\left[\omega_F \sum_{n=0}^{N} f_k^{(n)} e^{-i(\omega_F+\omega_{ext}n)t} + \sum_{n=0}^{N} n\omega_{ext} f_k^{(n)} e^{-i(\omega_F+\omega_{ext}n)t}\right] \\ = \sum_{n=0}^{N} E_k f_k^{(n)} e^{-i(\omega_F+\omega_{ext}n)t} + \sum_{m=\pm 1}\sum_{l} V_{kl}^{(m)} \sum_{n=0}^{N} f_l^{(p)} e^{-i(\omega_F+\omega_{ext}(p+m))t}.\end{aligned} \tag{2.6.7}$$

Now, we multiply the left-hand side of Eq. (2.6.7) by $\exp(i(\omega_F + \omega_{ext}n_0)t)$, where n_0 is a fixed integer, and integrate the obtained equation over time from 0 to T. This gives:

$$\hbar(\omega_F + n_0\omega_{ext}) f_k^{(n_0)} = E_k f_k^{(n_0)} + \sum_{l=1}^{2} \left(V_{kl}^{(1)} f_l^{(n_0-1)} + V_{kl}^{(-1)} f_l^{(n_0+1)}\right). \tag{2.6.8}$$

System of Eq. (2.6.8) is recurrent. Each of these equations connects three consecutive Fourier coefficients, $f_k^{(n_0)}$, $f_k^{(n_0-1)}$, and $f_k^{(n_0+1)}$. Generally, this system is infinite and is difficult to solve. However, within the rotating wave approximation (see Eq. (2.4.12)), the task can be simplified. In this approximation, the operator of the TLS interaction with the external field has the form:

$$\hat{V}(t) = \hbar\Omega_{ext}\left(\hat{\sigma}\exp(i\omega_{ext}t) + \hat{\sigma}^{\dagger}\exp(-i\omega_{ext}t)\right). \tag{2.6.9}$$

Using $\hat{\sigma} = |g\rangle\langle e|$ and $\hat{\sigma}^{\dagger} = |e\rangle\langle g|$, we can rewrite the matrix elements of the interaction operator as

$$V_{lk}(t) = \delta_{l1}\delta_{k2}V_{lk}^{(1)} \exp(-i\omega_{ext}t) + \delta_{l2}\delta_{k1}V_{lk}^{(-1)} \exp(i\omega_{ext}t), \tag{2.6.10}$$

where $V_{12}^{(1)} = V_{21}^{(-1)} = \hbar\Omega_{ext}$. After the substitution of Eq. (2.6.10) into Eq. (2.6.8), we obtain:

$$(\omega_F + n_0\omega_{ext})f_1^{(n_0)} = \left(E_1 f_1^{(n_0)} + V_{12}^{(1)} f_2^{(n_0-1)}\right)/\hbar, \tag{2.6.11}$$

$$(\omega_F + n_0\omega_{ext})f_2^{(n_0)} = \left(E_2 f_2^{(n_0)} + V_{21}^{(-1)} f_1^{(n_0+1)}\right)/\hbar. \tag{2.6.12}$$

We can see that each of the obtained equations connects only two unknowns. If we change the order of the equations, we can solve system (2.6.8). For this purpose, one should use the equation for the coefficients with the number $n_0 - 1$ instead of Eq. (2.6.12). The new equation,

$$(\omega_F + (n_0-1)\omega_{ext})f_2^{(n_0-1)} = \omega_2 f_2^{(n_0-1)} + V_{21}^{(-1)} f_1^{(n_0)}/\hbar, \tag{2.6.13}$$

contains the same variables as Eq. (2.6.11).

It is convenient to consider that in Eq. (2.2.11), the frequencies of the TLS ground and excited states are $\omega_2 = -\omega_\sigma/2$ and $\omega_1 = \omega_\sigma/2$, respectively. Using $V_{12}^{(-1)}/\hbar = V_{21}^{(-1)}/\hbar = \Omega$, we can rewrite Eqs. (2.6.11) and (2.6.13) in the form:

$$\begin{aligned}(\omega_F + n_0\omega_{ext})f_1^{(n_0)} &= \frac{\omega_\sigma}{2} f_1^{(n_0)} + \Omega_{ext} f_2^{(n_0-1)},\\ (\omega_F + (n_0-1)\omega_{ext})f_2^{(n_0-1)} &= -\frac{\omega_\sigma}{2} f_2^{(n_0-1)} + \Omega_{ext} f_1^{(n_0)}.\end{aligned} \tag{2.6.14}$$

As a result, we have a uniform system of two equations for two unknowns. This system of equations has a nontrivial solution if the frequency ω_F satisfies the characteristic equation:

$$(\omega_F + n_0\omega_{ext})^2 - (\omega_F + n_0\omega_{ext})\omega_{ext} - \left((\omega_\sigma/2)^2 - \omega_\sigma\omega_{ext}/2 + \Omega_{ext}^2\right) = 0 \tag{2.6.15}$$

The solution of this equation gives two Floquet's frequencies:

$$\omega_F^{(n_0,\pm)} = (-n_0\omega_{ext} + \omega_{ext}/2) \pm \Omega_\Delta, \tag{2.6.16}$$

where $\Omega_\Delta = \sqrt{\Omega_{ext}^2 + (\Delta_\omega/2)^2}$. Two eigenvectors, $f_1^{(n_0,\pm)}$ and $f_2^{(n_0-1,\pm)}$ corresponding to eigenfrequencies $\omega_F^{(n_0,\pm)}$, have the form:

$$\begin{pmatrix} f_1^{(n_0,+)} \\ f_2^{(n_0-1,+)} \end{pmatrix} = \begin{pmatrix} \frac{\Omega_\Delta + \Delta_\omega/2}{2\Omega_\Delta} \\ \frac{\Omega_\Delta - \Delta_\omega/2}{2\Omega_\Delta} \end{pmatrix}, \qquad \begin{pmatrix} f_1^{(n_0,-)} \\ f_2^{(n_0-1,-)} \end{pmatrix} = \begin{pmatrix} \frac{-\Omega_\Delta + \Delta_\omega/2}{2\Omega_\Delta} \\ \frac{\Omega_\Delta + \Delta_\omega/2}{2\Omega_\Delta} \end{pmatrix} \tag{2.6.17}$$

Using Eq. (2.6.5), we can find Floquet's eigensolution for fixed n_0. For the frequency $\omega_F^{(+)}$, it has the form:

$$\begin{aligned} |\psi(t)\rangle^{(+,n_0)} &= \frac{\Omega_\Delta + \Delta_\omega/2}{2\Omega_\Delta} \exp(-i(-n_0\omega_{ext} + \omega_{ext}/2 + \Omega_\Delta + n_0\omega_{ext})t)|e\rangle \\ &+ \frac{\Omega_\Delta - \Delta_\omega/2}{2\Omega_\Delta} \exp(-i(-n_0\omega_{ext} + \omega_{\mathrm{ext}}/2 + \Omega_\Delta + n_0\omega_{ext})t)|g\rangle \\ &= \frac{\Omega_\Delta + \Delta_\omega/2}{2\Omega_\Delta} \exp(-i(\omega_{ext}/2 + \Omega_\Delta)t)|e\rangle \\ &+ \frac{\Omega_\Delta + \Delta_\omega/2}{2\Omega_\Delta} \exp(-i(\omega_{ext}/2 + \Omega_\Delta)t)|g\rangle \equiv |\psi(t)\rangle^{(+)}. \end{aligned} \tag{2.6.18}$$

Similarly, for Floquet's frequency $\omega_F^{(-)}$, we obtain:

$$\begin{aligned} |\psi(t)\rangle^{(-)} &= \frac{-\Omega_\Delta + \Delta_\omega/2}{2\Omega_\Delta} \exp(-i(\omega_{ext}/2 - \Omega_\Delta)t)|e\rangle \\ &+ \frac{\Omega_\Delta + \Delta_\omega/2}{2\Omega_\Delta} \exp(-i(\omega_{ext}/2 - \Omega_\Delta)t)|g\rangle. \end{aligned} \tag{2.6.19}$$

One can see that the basis Floquet's states, Eqs. (2.6.18) and (2.6.19), do not depend on n_0. This is because the same solutions correspond to Floquet's frequencies that differ by $n\omega_{ext}$, where n is a number of the Floquet's solutions, $n < N$, (see Remark 2.5).

The general solution of the Schrödinger equation has the form:

$$\begin{aligned} |\psi(t)\rangle = c_1 &\frac{\Omega_\Delta + \Delta_\omega/2}{2\Omega_\Delta} \exp(-i\omega_{ext}t/2)\exp(-i\Omega_\Delta t)|e\rangle \\ + c_1 &\frac{\Omega_\Delta - \Delta_\omega/2}{2\Omega_\Delta} \exp(i\omega_{ext}t/2)(\exp(-i\Omega_\Delta t)|g\rangle) \\ + c_2 &\frac{-\Omega_\Delta + \Delta_\omega/2}{2\Omega_\Delta} \exp(-i\omega_{ext}t/2)\exp(i\Omega_\Delta t)|e\rangle \\ + c_2 &\frac{\Omega_\Delta + \Delta_\omega/2}{2\Omega_\Delta} \exp(i\omega_{ext}t/2)(\exp(i\Omega_\Delta t)|g\rangle), \end{aligned} \tag{2.6.20}$$

where coefficients $c_{1,\ 2}$ correspond to different Floquet's frequencies (see Eq. (2.6.16)) and are defined by initial conditions.

In the case of resonance, $\Delta_\omega = 0$, $\Omega_\Delta = \Omega_{ext}$, and $|\psi(0)\rangle = |g\rangle$, the solution to Eq. (2.6.20) has a simpler form:

$$|\psi(t)\rangle = -i\exp(-i\omega_{ext}t/2)\sin(\Omega_{ext}t)|e\rangle + \exp(i\omega_{ext}t/2)\cos(\Omega_{ext}t)|g\rangle. \quad (2.6.21)$$

For the expectation value of the inversion operator, we obtain:

$$\left\langle \hat{D}(t)\right\rangle = -\cos(2\Omega_{ext}t). \quad (2.6.22)$$

This is exactly the same expression we found using the Heisenberg approach (see Eq. (2.4.19)). Also, note that since $\left\langle \hat{D}(t)\right\rangle = \langle\psi(t)|\hat{D}|\psi(t)\rangle$, the frequency of the Rabi oscillations of the average value of the operator $\hat{D}$ is twice the frequency of the Rabi oscillations of the wave function.

To conclude, in this section we have illustrated that an atom interacting with a single classical EM mode forms a dressed atom—the closed Hermitian system with stationary states. If the atom interacts with a classical external field, the system state may be described as the Rabi oscillations of the population inversion. When an EM mode is quantized, the atom and the mode perform an endless periodic exchange of energy quanta (the Jaynes-Cummings states). For several modes, we observe a more complicated collapse-revival motion. In any case, the transition of an atom from one stationary state to another does not occur. This is the general property of closed Hermitian systems.

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Chapter 3
Open Quantum Systems

In this chapter, we show that to achieve a stationary state, a quantum system must interact with a reservoir of a continuum of modes. Dirac was the first to put forward this idea, which Fermi later used to derive a formula describing the probability of beta decay [1, 2]. This formula is known as Fermi's golden rule and is widely used in describing various quantum transitions. Since Fermi's golden rule results from using the first order of time-dependent perturbation theory, in specific cases, its application implies inevitable limitations, which are not always obvious and may lead to seeming contradictions to more detailed theories. Below, we clarify these limitations.

We begin with the Weisskopf-Wigner theory [3] of spontaneous emission, which shows that the interaction with a continuum of modes instead of a single mode prevents the endless periodic energy exchange. We will see that an excited atom interacting with empty reservoir of free space modes transitions irreversibly to the final state (the atom is in the ground state, and the reservoir of free space modes has one photon). The Weisskopf-Wigner theory predicts the dissipation rate in the initial moment and the frequency shift of the emitted radiation.

To consider the dynamics at larger times, we have to solve an infinite number of differential equations, which cannot be done without approximations. As mentioned in the Introduction, at large times, there are two ways to avoid dealing with an infinite number of degrees of freedom. These are using the Lindblad master equation and the Heisenberg-Langevin operator equations. These methods are outlined in this chapter.

At the end of the chapter, we show that the light emission of a quantum system is caused by the interaction with the reservoir of free space modes, and the spectrum of this radiation is associated with the perturbation of the reservoir.

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3.1 Spontaneous Radiation of a Two-Level System: Weisskopf-Wigner Approach

To consider spontaneous radiation, we follow the Weisskopf-Wigner approach. The approach assumes that a TLS interacts with the reservoir of free space modes. Moreover, the TLS and the reservoir form a closed Hermitian system with the Hamiltonian:

$$\hat{H} = \hbar\omega_\sigma \hat{\sigma}^+\hat{\sigma} + \sum_{\mathbf{k}} \hbar\omega_{a,\mathbf{k}} \hat{a}_{\mathbf{k}}^+ \hat{a}_{\mathbf{k}} + \sum_{\mathbf{k}} \hbar\Omega_{a,\mathbf{k}} \left(\hat{a}_{\mathbf{k}}^+ \hat{\sigma} + \hat{a}_{\mathbf{k}} \hat{\sigma}^+\right). \tag{3.1.1}$$

The first term in Eq. (3.1.1) represents the TLS Hamiltonian (2.2.11). The second term is the Hamiltonian of the quantized free space modes, which have eigenfrequencies $\omega_{a,\,\mathbf{k}}$:

$$\hat{H}_E = \sum_{\mathbf{k}} \hbar\omega_{a,\mathbf{k}} \hat{a}_{\mathbf{k}}^+ \hat{a}_{\mathbf{k}}, \tag{3.1.2}$$

and the third term is responsible for the interaction of these modes with the TLS:

$$\sum_{\mathbf{k}} \hbar\Omega_{\mathrm{a},\mathbf{k}} \left(\hat{a}_{\mathbf{k}}^+ \hat{\sigma} + \hat{a}_{\mathbf{k}} \hat{\sigma}^+\right) \tag{3.1.3}$$

$\Omega_{a,\mathbf{k}} = \sqrt{2\pi\omega_{a,\mathbf{k}}/\hbar V}\, \mathbf{e}_{\mathbf{k},\alpha} \cdot \mathbf{d}_{eg}$ is the coupling constant of the atom located in the point $\mathbf{r}_0$ with the photon mode, which has the eigenfrequency $\omega_{a,\,\mathbf{k}}$ and the wave vector $\mathbf{k}$, where $|\mathbf{k}| = \omega_{a,\,\mathbf{k}}/c$.

Let us assume that at the initial moment, $t = 0$, the TLS is in the excited state $|e, 0\rangle$, and there are no photons in the free space. Then, at subsequent moments of time, the wave function $|\Psi(t)\rangle$ of the system, which includes the TLS and photons in free space modes, can be represented in the form:

$$|\Psi(t)\rangle = C_e(t) e^{-i\omega_\sigma t} |e, 0\rangle + \sum_{\mathbf{k}} C_{g,\mathbf{k}}(t) e^{-i\omega_{a,\mathbf{k}} t} |g, 1_{\mathbf{k}}\rangle, \tag{3.1.4}$$

where $C_e(0) = 1$, $C_{g,\,\mathbf{k}}(0) = 0$, and $|g, 1_{\mathbf{k}}\rangle$ is the system state in which the TLS is in the ground state, while there is one photon with the wave vector $\mathbf{k}$ in free space.

Our goal is to find the states of the TLS and the photon after a certain time t when the TLS emits a photon. Substituting Eqs. (3.1.1) and (3.1.4) into the Schrödinger equation and scalar multiplying by $\langle 0, e|$ and $\langle 1_{\mathrm{k}}, g|$, we obtain the equations of motion for the probability amplitudes $C_e(t)$ and $C_{g,\,\mathbf{k}}(t)$:

$$\frac{dC_e(t)}{dt} = -i \sum_{\mathbf{k}} \Omega_{a,\mathbf{k}} e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})t} C_{g,\mathbf{k}}(t), \tag{3.1.5}$$

$$\frac{dC_{g,\mathbf{k}}(t)}{dt} = -i\Omega_{a,\mathbf{k}} e^{-i(\omega_\sigma - \omega_{a,\mathbf{k}})t} C_e(t). \tag{3.1.6}$$

To eliminate the variables $C_{g,\,\mathbf{k}}(t)$ from Eq. (3.1.5), we integrate Eq. (3.1.6) over time with the initial conditions $C_e(0) = 1$ and $C_{g,\,\mathbf{k}}(0) = 0$. This gives:

$$C_{g,\mathbf{k}}(t) = -i\Omega_{a,\mathbf{k}} \int_0^t dt' e^{-i(\omega_\sigma - \omega_{a,\mathbf{k}})t'} C_e(t'). \tag{3.1.7}$$

Changing variables in Eq. (3.1.7) from t' to $\tau = t - t'$, we obtain:

$$C_{g,\mathbf{k}}(t) = -i\Omega_{a,\mathbf{k}} e^{-i(\omega_\sigma - \omega_{a,\mathbf{k}})t} \int_0^t d\tau e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})\tau} C_e(t-\tau). \tag{3.1.8}$$

Substituting Eq. (3.1.8) into Eq. (3.1.5), we obtain an equation containing only one variable $C_e(t)$:

$$\dot{C}_e(t) = -\sum_{\mathbf{k}} \Omega_{a,\mathbf{k}}^2 \int_0^t d\tau e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})\tau} C_e(t-\tau). \tag{3.1.9}$$

Thus, we replace infinite system of differential eqs. (3.1.5)–(3.1.6) with single integro-differential eq. (3.1.9) from which all the variables $C_{g,\,\mathbf{k}}(t)$ are excluded. Equation (3.1.9) for $C_e(t)$ is still exact; it cannot be solved analytically. To obtain a solution to this equation, we use the Markov approximation, which allows for the substitution of $C_e(t-\tau)$ by $C_e(t)$ in Eq. (3.1.9). Then, Eq. (3.1.9) reduces to a simpler equation:

$$\frac{dC_e(t)}{dt} = -\left(\gamma^{(rad)}/2\right) C_e(t), \tag{3.1.10}$$

where

$$\gamma^{(rad)}/2 = \sum_{\mathbf{k}} \Omega_{a,\mathbf{k}}^2 \int_0^t d\tau e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})\tau}.$$

Consequently, the probability of an atom being in the excited state, $P_e(t) = |C_e(t)|^2$, changes in time according to the equation $dP_e/dt = -\gamma^{(rad)} P_e$.

When solving Eq. (3.1.9), we assume that $\omega_\sigma^{-1} \ll t \ll \left(\gamma^{(rad)}\right)^{-1}$, where $(\gamma^{(rad)})^{-1}$ is the characteristic time at which the value of $C_e(t)$ changes. This assumption is based on the experiments showing that the decay is a slow process, in the sense that

the decay rate is much smaller than the transition frequency ω_σ. In theory, the latter inequality reflects the weakness of the interaction of an atom with the reservoir of EM free space modes.

The validity of this approximation must be checked at the end of the calculations. For times $t < \tau$, during which $C_e(t-\tau)$ changes only slightly, it can be expanded in the Taylor series:

$$C_e(t-\tau) \simeq C_e(t) - \tau \frac{dC_e(t)}{dt}.$$

Substituting this expansion into Eq. (3.1.9), we obtain:

$$\begin{aligned}\frac{dC_e(t)}{dt} &\simeq -\sum_{\mathbf{k}} \Omega_{a,\mathbf{k}}^2 \int_0^t d\tau e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})\tau} \left(C_e(t) - \tau \dot{C}_e(t)\right) \\ &= -\sum_{\mathbf{k}} \Omega_{a,\mathbf{k}}^2 C_e(t) \int_0^t d\tau e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})\tau} + \sum_{\mathbf{k}} \Omega_{a,\mathbf{k}}^2 \frac{dC_e(t)}{dt} \int_0^t d\tau e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})\tau} \tau.\end{aligned} \tag{3.1.11}$$

Given that $t \ll \left(\gamma_D^{(rad)}\right)^{-1}$, we obtain:

$$\begin{aligned}\left|\frac{dC_e(t)}{dt} \int_0^t d\tau e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})\tau} \tau\right| &\simeq \left|C_e(t) \frac{\gamma^{(rad)}}{2} \int_0^t d\tau e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})\tau} \tau\right| \le \left|C_e(t) \frac{\gamma^{(rad)}}{2} t \int_0^t d\tau e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})\tau}\right| \\ &= \frac{\gamma^{(rad)}}{2} t \left|C_e(t) \int_0^t d\tau e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})\tau}\right| \ll \left|C_e(t) \int_0^t d\tau e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})\tau}\right|.\end{aligned} \tag{3.1.12}$$

Thus, in the leading order of the perturbation theory in the small parameter $\gamma_D^{(rad)} t$, the second term on the right-hand side of Eq. (3.1.11) can be omitted because it is much smaller than the first term. This confirms our assumption (3.1.10). Then, Eq. (3.1.11) is transformed into

$$\frac{dC_e(t)}{dt} = -\sum_{\mathbf{k}} \Omega_{a,\mathbf{k}}^2 C_e(t) \int_0^t d\tau e^{i(\omega_\sigma - \omega_{a,\mathbf{k}})\tau}. \tag{3.1.13}$$

The integrand in Eq. (3.1.13) oscillates rapidly; therefore, the main contribution to the integral comes from the time interval $\tau \le 1/\omega_\sigma$. Since we consider times $t \gg 1/\omega_\sigma$, we can extend the upper limit of integration to ∞. Finally, we obtain:

$$\frac{dC_e(t)}{dt} = -C_e(t)\sum_{\mathbf{k}}\Omega_{a,\mathbf{k}}^2\int_0^\infty d\tau e^{-i(\omega_\sigma-\omega_{a,\mathbf{k}})\tau}. \tag{3.1.14}$$

To calculate the integral in Eq. (3.1.14), we introduce the term $(-\varepsilon\tau)$ into the argument of the exponent; in the end, ε is set to zero:

$$\begin{aligned}\lim_{\varepsilon\to 0}\int_0^\infty d\tau e^{i(\omega_\sigma-\omega_{a,\mathbf{k}})\tau-\varepsilon\tau} &= \lim_{\varepsilon\to 0}\frac{i}{\omega_{a,\mathbf{k}}-\omega_\sigma+i\varepsilon}\\ &= i\left[\mathcal{P}\left(\frac{1}{\omega_{a,\mathbf{k}}-\omega_\sigma}\right)-i\pi\delta(\omega_{a,\mathbf{k}}-\omega_\sigma)\right].\end{aligned} \tag{3.1.15}$$

The δ-function in Eq. (3.1.15) indicates that a photon is emitted into the modes whose frequencies are equal to the transition frequency of the atom. In the last step, we use the Sokhotski formula:

$$\lim_{\varepsilon\to 0}\frac{1}{x\pm i\varepsilon} = \mathcal{P}\left(\frac{1}{x}\right)\mp i\pi\delta(x), \tag{3.1.16}$$

where $\mathcal{P}$ denotes the principal value of the integral.

Substituting Eq. (3.1.15) into Eq. (3.1.14), we obtain:

$$\frac{dC_e(t)}{dt} = -\left(\frac{\gamma^{(rad)}}{2}+i\Delta\omega\right)C_e(t), \tag{3.1.17}$$

where

$$\gamma^{(rad)}/2 = \pi\sum_{\mathbf{k}}\Omega_{a,\mathbf{k}}^2\delta(\omega_{a,\mathbf{k}}-\omega_\sigma), \tag{3.1.18}$$

The quantity

$$\Delta\omega = \sum_{\mathbf{k}}\frac{\Omega_{a,\mathbf{k}}^2}{\omega_{a,\mathbf{k}}-\omega_\sigma} \tag{3.1.19}$$

is a correction to the oscillation frequency of $C_e(t)$. This correction, called the Lamb shift, is due to the TLS interaction with the reservoir.

In Eqs. (3.1.18) and (3.1.19), it is convenient to replace the summation over the wave vectors with the integration over the frequency, $\sum_{\mathbf{k}}\to\int d\omega\Pi(\omega)$. Here, $\Pi(\omega)$, the number of states per unit frequency interval, has the form [4]:

$$\Pi(\omega) = \frac{V\omega^2}{\pi^2 c^3}. \tag{3.1.20}$$

Transitioning to the integration over the frequency and taking into account that $\Omega_{a,\mathbf{k}}^2 \sim \sin^2\theta$ converts Eq. (3.1.18) into the following expressions for the dissipation rate (see Problem 1.6, Eq. (6.14)):

$$\gamma^{(rad)}/2 = \int d\omega \frac{2\pi}{3}\Omega_a^2(\omega)\Pi(\omega)\delta(\omega-\omega_\sigma) = \frac{2\pi}{3}\Omega_a^2(\omega_\sigma)\Pi(\omega_\sigma), \tag{3.1.21}$$

where the factor $2\pi/3$ comes from the integration over the solid angle and the summation over polarizations. Similarly, for the Lamb shift, we obtain:

$$\Delta\omega = V\mathcal{P}\int d\omega \frac{\Pi(\omega)\Omega_a^2(\omega)/3}{\omega-\omega_\sigma}. \tag{3.1.22}$$

To evaluate the values $\gamma^{(rad)}$ and $\Delta\omega^{-1}$ from Eq. (3.1.17), we need to calculate the coupling constants $\Omega_{a,\,\mathbf{k}}$ of the interaction of an atomic dipole moment with the electric field of the free space modes and substitute them into Eqs. (3.1.18) and (3.1.19). This leads us to the following expression (see Problem 1.6):

$$\gamma^{(rad)} = \frac{4}{3}\frac{\left|\mathbf{d}_{eg}\right|^2\omega_\sigma^3}{\hbar c^3}. \tag{3.1.23}$$

Since the atomic dipole moment d_{eg} is of the order of ea_B, where $a_B \sim \hbar^2/me^2$ is the Bohr radius, we arrive at the following expression for $\gamma^{(rad)}$:

$$\gamma^{(rad)} \sim \alpha^3\omega_\sigma \sim 10^{-6}\omega_\sigma \ll \omega_\sigma, \tag{3.1.24}$$

where $\alpha = e^2/\hbar c \approx 1/137$ is the fine-structure constant. Thus, our initial assumption that spontaneous emission is a "slow" process is valid.

The expression for the shift of the transition frequency of the atom is obtained in a similar way:

$$\Delta\omega = \frac{2\left|\mathbf{d}_{eg}\right|^2\omega_\sigma^3}{3\pi\hbar c^3}\int_0^\infty \mathcal{P}\left(\frac{1}{\omega_{a,\mathbf{k}}-\omega_\sigma}\right)d\omega_{a,\mathbf{k}}. \tag{3.1.25}$$

This is the Lamb shift of the TLS transition frequency (the frequency of the center of the emission line). In Eq. (3.1.25), the integral diverges. This divergence arises due to the inapplicability of the nonrelativistic Jaynes-Cummings Hamiltonian at high frequencies when the photons emitted by TLS can produce virtual electron-positron pairs with the energy $\hbar\omega_{a,\,\mathbf{k}} \approx 2mc^2$, where m is the mass of the electron. (This process is often called "knocking out from the vacuum.") An accurate calculation of

the Lamb shift can only be carried out by using methods of quantum electrodynamics that allow for taking relativistic and radiation corrections into account [5]. Nevertheless, an estimation for $\Delta\omega$ could be obtained by cutting off the integral in Eq. (3.1.25) at the frequency $\omega_{a,\,\mathbf{k}} \approx \hbar^{-1}2mc^2$. The resulting expression,

$$\Delta\omega = \frac{2\left|\mathbf{d}_{eg}\right|^2\omega_\sigma^3}{3\pi\hbar c^3}\ln\left(\frac{2mc^2}{\hbar\omega_\sigma}\right), \tag{3.1.26}$$

differs from the prediction of quantum electrodynamics by a numerical factor only (see Problem 1.6). The Lamb shift lies in the microwave range, $\Delta\omega \sim \gamma^{(rad)} \ll \omega_\sigma$. This justifies the Weisskopf-Wigner approximation.

Thus, the probability of finding a TLS in an excited state decreases exponentially:

$$|C_e(t)|^2 = \exp\left(-\gamma^{(rad)}t\right) \tag{3.1.27}$$

with the characteristic lifetime $\tau = 1/\gamma^{(rad)}$. Equation (3.1.27) shows that the initial excitation dissipates into the reservoir of free space modes. In accordance with the fluctuation-dissipation theorem, the presence of dissipation requires that, along with dissipation, a noise term is introduced into eqs. [6]. To obtain such a term, much more complicated calculations are required. These calculations are discussed in Sect. 3.2.

To summarize, in this section, we have shown that the presence of a continuum of reservoir modes with a given energy and all possible directions of wave vectors is a sufficient condition for the irreversibility of the transition of an atom from an excited state to a ground state. The summation of the feedback of the continuum of modes shows the decay of the excited atom state (see Eq. (3.1.14)). The integral in this equation has a real part, which is responsible for the irreversible relaxation.

It is generally recognized that if a reservoir has a Hamiltonian with a discrete spectrum, the population of the excited level of a TLS is quasi-periodic in time [7] and does not have a limit as $t \to \infty$. However, if the Hamiltonian spectrum contains continuum parts, the population of the excited level can tend to a limit state.

In Refs. [8–10], by using a simple model, it was also shown that in systems with discrete spectra, the complicated quasiperiodic oscillations start after a characteristic time τ_H. Before this time, the system exhibits overdamped oscillations and quasi-exponential decay of excitation. The time τ_H increases as the spectrum becomes denser. When continuum regions appear in the energy spectrum, the evolution operator becomes non-unitary and τ_H tends to infinity. In this sense, the motion of such systems can be termed "irreversible." Thus, for a transition of an atom from one state to another with loss or absorption of a quantum of energy to be irreversible, the final state should belong to a reservoir with an infinite number of degrees of freedom.

Generally, one cannot solve an infinite number of Heisenberg or Schrödinger equations, which include all reservoir variables. Therefore, to describe the systems, we should obtain new equations, which only include essential variables belonging to the atom and incident photons. Such a subsystem is called open.

For this purpose, we should eliminate the reservoir variables from the complete set of the Heisenberg or Schrödinger equations. The resulting equations differ from the Heisenberg and Schrödinger equations. In particular, as shown below, such equations are not Hermitian and contain dissipation and noise terms. The latter terms reflect the coupling of the open system with the reservoir. We show that eliminating the reservoir variables can be achieved when the Markov and Born approximations are applicable.

3.2 Application of the Lindblad Equation for Radiation Problem

In the previous section, we showed that spontaneous emission is possible if a TLS interacts with an infinite reservoir of free space modes. We also mentioned two methods to deal with a system interacting with a reservoir with an infinite number of degrees of freedom—the method of Heisenberg-Langevin operator equations in the Heisenberg picture and the Lindblad equation in the Schrödinger picture.

Although the derivation of the Heisenberg-Langevin operator equations is rather transparent, the solution of the equations and interpretations of the results may require substantial effort because we should transition from operators to *c*-numbers, i.e., to expectation values of operators. In this sense, the Schrödinger picture is preferable.

In the next subsections, we discuss a practical approach to dealing with an open system that employs the Schrödinger picture.

3.2.1 The Density Matrix: von Neumann Equation

Suppose we can divide the total system into two subsystems—a small subsystem (an open system) and a large subsystem (a reservoir). We denote the set of coordinates of the small subsystem by $\mathbf{x}$ and the set of coordinates of the reservoir by $\mathbf{q}$. In the Schrödinger picture, information about all properties of a closed Hermitian system is contained in the wave function $\Psi(\mathbf{x}, \mathbf{q})$. We are interested in some physical quantity f of the open system. The quantum operator $\hat{f}_{\mathbf{x}}$, which corresponds to f, acts on the variables $\mathbf{x}$ only.

The expectation value $\langle \hat{f}_{\mathbf{x}} \rangle$ can be found by the usual formula for total closed systems:

$$\langle \hat{f}_{\mathbf{x}} \rangle = \int d\mathbf{q} \int d\mathbf{x} \Psi^*(\mathbf{x}, \mathbf{q}) \hat{f}_{\mathbf{x}} \Psi(\mathbf{x}, \mathbf{q}) \tag{3.2.1}$$

To proceed, it is convenient to introduce a density matrix:

$$\rho(\mathbf{x}, \mathbf{x}') = \int d\mathbf{q} \Psi(\mathbf{x}, \mathbf{q}) \Psi^*(\mathbf{x}', \mathbf{q}), \tag{3.2.2}$$

which depends on the coordinates of the small subsystem but also contains information about the reservoir. We show that knowing $\rho(\mathbf{x}, \mathbf{x}')$, we can calculate the expectation values of any physical property f of a small subsystem.

The expectation value $\langle \hat{f}_{\mathbf{x}} \rangle$ can be expressed as

$$\begin{aligned} \langle \hat{f}_{\mathbf{x}} \rangle &= \int d\mathbf{x} d\mathbf{x}' \delta(\mathbf{x} - \mathbf{x}') \int d\mathbf{q} \Psi^*(\mathbf{x}', \mathbf{q}) \hat{f}_{\mathbf{x}} \Psi(\mathbf{x}, \mathbf{q}) \\ &= \int d\mathbf{x} d\mathbf{x}' \delta(\mathbf{x} - \mathbf{x}') \hat{f}_{\mathbf{x}} \int d\mathbf{q} \Psi(\mathbf{x}, \mathbf{q}) \Psi^*(\mathbf{x}', \mathbf{q}) \\ &= \int d\mathbf{x} \int d\mathbf{x}' \delta(\mathbf{x} - \mathbf{x}') \hat{f}_{\mathbf{x}} \rho(\mathbf{x}, \mathbf{x}') = \int d\mathbf{x} \hat{f}_{\mathbf{x}} \rho(\mathbf{x}, \mathbf{x}) = Tr\left[\hat{f}_{\mathbf{x}} \rho\right] \end{aligned} \tag{3.2.3}$$

Certainly, $\langle \hat{f}_{\mathbf{x}} \rangle$ depends on the state of the reservoir. This is why we call the small subsystem open.

If the subsystem and the reservoir do not interact, the wave function $\Psi(\mathbf{q}, \mathbf{x})$ of the total system is the product $\Psi_{OS}(\mathbf{x})\Psi_R(\mathbf{q})$, and the density matrix is reduced to $\hat{\rho}(\mathbf{q}, \mathbf{q}') = \Psi(\mathbf{q})\Psi^*(\mathbf{q}')$ or in the Dirac notations:

$$\hat{\rho} = |\Psi\rangle\langle\Psi|. \tag{3.2.4}$$

By taking a derivative over time, we obtain the equation of motion:

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar}\left(\hat{H}\hat{\rho} - \hat{\rho}\hat{H}\right) = -\frac{i}{\hbar}\left[\hat{H}, \hat{\rho}\right], \tag{3.2.5}$$

which is known as the von Neumann equation for the density matrix.

In the case of interacting subsystems, the Lindblad equation is used instead of the von Neumann equation; we proceed to deriving the former equation in the next subsection.

3.2.2 Derivation of the Lindblad Equation for the Density Matrix of an Open System

Now, we return to our problem in which a closed system is separated into the open system S and the reservoir R. The Hamiltonian of the closed system $H = H_S + H_R + H_{SR}$ consists of the Hamiltonians H_S, H_R, and H_{SR} describing the open system, the reservoir, and the interaction of the subsystems, respectively.

We analyze the evolution of the open system S by using its density matrix ρ_S. To find ρ_S, we need to average the density matrix of the closed system over the reservoir states $\hat{\rho}_S(t) = Tr_R(\hat{\rho}(t))$. The matrix $\hat{\rho}_S(t)$ depends on the system degrees of freedom only. Then, the expectation value of any operator $\hat{F}_S$, which acts on S only, is simply expressed as $\langle \hat{F}_S \rangle = Tr_S(\hat{\rho}_S \hat{F}_S)$. However, due to the interaction of the system S with the reservoir, the density matrix $\hat{\rho}_S(t) = Tr_R(\hat{\rho}(t))$ is *not* governed by the von Neumann equation in which only the system Hamiltonian is taken into account:

$$\frac{\partial \hat{\rho}_S}{\partial t} = -\frac{1}{i\hbar}[H_S, \rho_S].$$

Our task is to derive the equation of motion for $\hat{\rho}_S(t)$, which is usually referred to as the Lindblad equation.

If the quantum system S is closed, its dynamics is described by the Schrödinger equation. When the system interacts with an environment, e.g., with the reservoir R, the system becomes a subsystem of the closed system that includes the reservoir. The *ab initio* approach for calculating the dynamics of the system S has to use the solution to the Schrödinger equation for the whole closed system averaged over the reservoir variables. In practice, such an approach often cannot be realized because the number of degrees of freedom of the reservoir is typically very large. Hence, the question arises as to whether it is possible to construct a closed equation that would only describe the system S dynamics. This can be done in the Born-Markov approximation (see Remark 3.1 and Refs. [11–13]). Below, using the apparatus of the density matrix, we derive the corresponding equations [7, 14].

Remark 3.1 **Born-Markov approximation**. The Born approximation assumes that when an external force is exerted on a system, the force does not change. In other words, we neglect the feedback effect of the system on the impact. In particular, while considering the interaction of a system with a reservoir of a large number of degrees of freedom, we assume that the reservoir state does not change.

The Markov approximation assumes neglecting the entire history of the system's evolution up to a given moment, and the immediate future state of the system is completely determined by its present state.

The dynamics of an open system S can be described by the density matrix $\hat{\rho}_S$. It is also convenient to describe the dynamics of the closed system by the density matrix $\hat{\rho}$. The latter obeys the von Neumann equation for the density matrix $\hat{\rho}$ [13, 15]:

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_S + \hat{H}_R + \hat{H}_{SR}, \hat{\rho}(t)\right]. \tag{3.2.6}$$

We confine ourselves to the interaction Hamiltonian of the following form:

$$\hat{H}_{SR} = \hbar\kappa \hat{S}\hat{R}, \tag{3.2.7}$$

where $\hat{S}$ and $\hat{R}$ are operators that only depend on the dynamic variables of the system and the reservoir, respectively, and κ is the coupling constant of the system with the reservoir. In what follows, the operators $\hat{S}$ and $\hat{R}$ are dimensionless, and Planck's constant in the expression for $\hat{H}_{SR}$ is introduced so that the coupling constant κ has the dimension of frequency. Though this is not the general form of the interaction Hamiltonians, all the Hamiltonians we use in Part I of this book have this form, e.g., the interaction Hamiltonian of a TLS with the reservoir of the free space modes or with the reservoir of phonons. We assume that the operators $\hat{S}$ and $\hat{R}$ correspond to some observable physical quantity and are Hermitian.

Since we imply that the interaction is of the EM nature, the coupling constant κ is small compared to the atomic eigenfrequencies; the typical ratio of these quantities is proportional to the fine-structure constant $\alpha \approx 1/137 \ll 1$ [16]. Thus, $\kappa \ll \Delta\omega_S$, where $\Delta\omega_S$ is the characteristic frequency difference between the system eigenstates. It means that the dynamics of open system S is described by two different time scales: a short time scale $\sim(\Delta\omega_S)^{-1}$, which characterizes the internal interactions inside the system, and a long time scale $\sim 1/\kappa$ that characterizes the relaxation of the system S. We are mainly interested in the processes that happen at the time scale:

$$(\Delta\omega_S)^{-1} < \Delta t < 1/\kappa. \tag{3.2.8}$$

As has been mentioned above, to study the dynamics of the open system S, we exclude all variables belonging to the reservoir from Eq. (3.2.6). For this purpose, we use the interaction picture:

$$\widehat{\widehat{\rho}}(t) = \exp\left(i\left(\hat{H}_S + \hat{H}_R\right)t/\hbar\right)\hat{\rho}\exp\left(-i\left(\hat{H}_S + \hat{H}_R\right)t/\hbar\right).$$

In this picture, the density matrix $\widehat{\widehat{\rho}}(t)$ satisfies the equation:

$$\frac{\partial \widehat{\widehat{\rho}}(t)}{\partial t} = -\frac{i}{\hbar}\left[\widehat{\widehat{H}}_{SR}(t), \widehat{\widehat{\rho}}\right], \tag{3.2.9}$$

where

$$\widehat{\widetilde{H}}_{SR}(t) = \exp\left(i\left(\hat{H}_S + \hat{H}_R\right)t/\hbar\right)\hat{H}_{SR}\exp\left(-i\left(\hat{H}_S + \hat{H}_R\right)t/\hbar\right).$$

Note that $\left[\hat{S}, \hat{R}\right] = 0$ and $\left[\hat{H}_S, \hat{H}_R\right] = 0$. The operators $\hat{S}$ and $\hat{R}$, as well as the Hamiltonians $\hat{H}_S$ and $\hat{H}_R$, commute because these operators correspond to different degrees of freedom. Then, in the interaction picture, the operator $\hat{H}_{SR} = \hbar\kappa\hat{S}\hat{R}$ can be rewritten in the form:

$$\widehat{\widetilde{H}}_{SR}(t) = \hbar\kappa\widehat{\widetilde{S}}(t)\widehat{\widetilde{R}}(t) \tag{3.2.10}$$

where

$$\widehat{\widetilde{S}}(t) = \exp\left(i\hat{H}_S t/\hbar\right)\hat{S}\exp\left(-i\hat{H}_S t/\hbar\right)$$

and

$$\widehat{\widetilde{R}}(t) = \exp\left(i\hat{H}_R t/\hbar\right)\hat{R}\exp\left(-i\hat{H}_R t/\hbar\right).$$

The coupling constant in the interaction operator $\widehat{\widetilde{H}}_{SR}(t)$ is still equal to κ.

Equation (3.2.9) may be recast as

$$\frac{\partial\widehat{\widetilde{\rho}}(t)}{\partial t} = -i\kappa\left[\widehat{\widetilde{S}}(t)\widehat{\widetilde{R}}(t), \widehat{\widetilde{\rho}}\right] \tag{3.2.11}$$

It is worth emphasizing that in the interaction picture, both operators and wave functions may depend upon time. Equation (3.2.11) shows that in the interaction picture, when $\kappa = 0$, the density matrix does not depend on time, $\widehat{\widetilde{\rho}}(t) = \text{constant}$.

To move on, we use the unitary time evolution operator determined by the equation:

$$\left|\widetilde{\Psi}(t_0 + \Delta t)\right\rangle = \hat{U}(t_0 + \Delta t, t_0)\left|\widetilde{\Psi}(t_0)\right\rangle \tag{3.2.12}$$

with $\hat{U}(t_0, t_0, \kappa) = \hat{I}$ and $\widehat{\widetilde{U}}(t, t_0, \kappa = 0) = \hat{I}$. Here $\left|\widetilde{\Psi}(t)\right\rangle$ is an arbitrary wave function that is governed by the Schrödinger equation $\widehat{\widetilde{H}}_{SR}\left|\widetilde{\Psi}(t)\right\rangle = i\hbar\partial\left|\widetilde{\Psi}(t)\right\rangle/\partial t$. Substituting the wave function in the form (3.2.12) into the Schrödinger equation, we obtain the relationship:

$$i\hbar\frac{\partial\hat{U}(t, t_0)}{\partial t}\left|\widetilde{\Psi}(t_0)\right\rangle = \widehat{\widetilde{H}}_{SR}\hat{U}(t, t_0)\left|\widetilde{\Psi}(t_0)\right\rangle.$$

Due to the arbitrariness of the wave function $|\Psi(t_0)\rangle$, we obtain the equation for $\hat{U}(t,t_0)$:

$$i\hbar\frac{\partial\hat{U}(t,t_0)}{\partial t}=\hat{\tilde{H}}_{SR}\hat{U}(t,t_0). \tag{3.2.13}$$

By integrating Eq. (3.2.13) over time, we arrive at the expression suitable for the application of the perturbation theory:

$$\hat{U}^{(n+1)}(t_0+\Delta t,t_0)=\hat{I}-\frac{i}{\hbar}\int\limits_{t_0}^{t_0+\Delta t}dt_1\hat{\tilde{H}}_{SR}\hat{U}^{(n)}(t_1,t_0). \tag{3.2.14}$$

with $\hat{U}^{(0)}(t,t_0)=\hat{U}(t,t_0,\kappa=0)=\hat{I}$. As mentioned above, we are mainly interested in the processes that occur on times $(\Delta\omega_S)^{-1}<\Delta t<1/\kappa$.

Using explicit expression (3.2.10) for $\hat{\tilde{H}}_{SR}$, we can obtain a series expansion for $\hat{U}^{(n+1)}(t,t_0)$:

$$\begin{aligned}
&\hat{U}^{(n+1)}(t,t_0)\\
&=\hat{1}+(-i\kappa\Delta t)^1\left(\frac{1}{\Delta t}\right)\int\limits_{t_0}^{t}dt_1\hat{\tilde{S}}(t_1)\hat{\tilde{R}}(t_1)\\
&\quad+(-i\kappa\Delta t)^2\left(\frac{1}{\Delta t}\right)\int\limits_{t_0}^{t}dt_1\hat{\tilde{S}}(t_1)\hat{\tilde{R}}(t_1)\left(\frac{1}{\Delta t}\right)\int\limits_{t_0}^{t_1}dt_2\hat{\tilde{S}}(t_2)\hat{\tilde{R}}(t_2)\ +\ \ldots\\
&\quad+(-i\kappa\Delta t)^{n+1}\left(\frac{1}{\Delta t}\right)\int\limits_{t_0}^{t}dt_1\hat{\tilde{S}}(t_1)\hat{\tilde{R}}(t_1)\times\ \ldots\ \times\left(\frac{1}{\Delta t}\right)\int\limits_{t_0}^{t_n}dt_{n+1}\hat{\tilde{S}}(t_{n+1})\hat{\tilde{R}}(t_{n+1})\hat{U}(t_{n+1},t_0)
\end{aligned} \tag{3.2.15}$$

where Δt is a characteristic time of the order of $\sim t-t_0$.

In the limit $n\to\infty$, the last term tends to zero. Indeed, if the operator $\hat{\tilde{H}}_{SR}(t)$ is bounded i.e., for any moment of time, in any basis, the absolute value of any matrix elements of $\hat{\tilde{H}}_{SR}(t)$ is limited from above by a finite value $H_{\max}$. Then, by definition, the evolution operator is also always bounded. (This is correct until the times considered are smaller than the time of returning of excitation from the reservoir to the system [17, 18].) Consequently, the last term in Eq. (3.2.15) can be evaluated as[1]

[1] For large n, we have used the Stirling approximation $n\,!\sim(n/e)^n$.

$$\left|(-i/\hbar)^{n+1}\int_{t_0}^{t}dt_1\widehat{\widehat{H}}_{SR}(t_1)\ldots\int_{t_0}^{t_{n-1}}dt_n\widehat{\widehat{H}}_{SR}(t_n)\int_{t_0}^{t_n}dt_{n+1}\widehat{\widehat{H}}_{SR}(t_{n+1})\hat{U}(t_{n+1})\right|$$
$$\leq\kappa^{n+1}\left\langle\hat{S}\hat{R}\right\rangle_{\max}\int_{t_0}^{t}dt_1\ldots\int_{t_0}^{t_{n-1}}dt_n\int_{t_0}^{t_n}dt_{n+1} \tag{3.2.16}$$
$$\simeq\frac{\kappa^{n+1}(t-t_0)^{n+1}}{(n+1)!}\simeq\left(\kappa\frac{(t-t_0)e}{(n+1)}\right)^{n+1}$$

Here, we evaluate the maximal expectation value of $\left\langle\hat{S}\hat{R}\right\rangle_{\max}$ as $O(1)$ because $\hat{S}$ and $\hat{R}$ are dimensionless operators. One can see that for any fixed t, the last term in Eq. (3.2.15) tends to zero when $n\to\infty$.

In the next step, taking into account the smallness of $\kappa\Delta t$, in Eq. (3.2.15), we retain terms that are only of the first or second order in the coupling constant κ:

$$\hat{U}(t+\Delta t,t_0)\approx 1-i(\kappa\Delta t)\left(\frac{1}{\Delta t}\right)\int_{t_0}^{t+\Delta t}\widehat{\widehat{S}}(t_1)\widehat{\widehat{R}}(t_1)dt_1$$
$$-(\kappa\Delta t)^2\left(\frac{1}{\Delta t}\right)\int_{t_0}^{t+\Delta t}dt_1\left(\frac{1}{\Delta t}\right)\int_{t_0}^{t_1}\left(\widehat{\widehat{S}}(t_1)\widehat{\widehat{R}}(t_1)\right)\left(\widehat{\widehat{S}}(t_2)\widehat{\widehat{R}}(t_2)\right)dt_2 \tag{3.2.17}$$

Taking into account that $\widehat{\widehat{\rho}}(t_0)=|\Psi(t_0)\rangle\langle\Psi(t_0)|$, to describe the evolution of the density matrix, instead of Eq. (3.2.12), we use:

$$\widehat{\widehat{\rho}}(t_0+\Delta t)=\hat{U}(t_0+\Delta t,t_0)\widehat{\widehat{\rho}}(t_0)\hat{U}^{\dagger}(t_0+\Delta t,t_0) \tag{3.2.18}$$

We now substitute Eq. (3.2.17) into Eq. (3.2.18) to obtain

$$\widehat{\widehat{\rho}}(t_0+\Delta t)=\widehat{\widehat{\rho}}(t_0)+\kappa\widehat{\widehat{\rho}}_1(t_0+\Delta t)+\kappa^2\widehat{\widehat{\rho}}_2(t_0+\Delta t), \tag{3.2.19}$$

where we introduce the notations

$$\widehat{\widehat{\rho}}_1(t_0+\Delta t)=-i\int_{t_0}^{t_0+\Delta t}\widehat{\widehat{S}}(t_1)\widehat{\widehat{R}}(t_1)dt_1\widehat{\widehat{\rho}}(t_0)+\widehat{\widehat{\rho}}(t_0)i\int_{t_0}^{t_0+\Delta t}\widehat{\widehat{S}}(t_1)\widehat{\widehat{R}}(t_1)dt_1 \tag{3.2.20}$$

$$\begin{aligned}\widehat{\widetilde{\rho}}_2(t_0+\Delta t) = &\int_{t_0}^{t_0+\Delta t} \widehat{\widetilde{S}}(t_1)\widehat{\widetilde{R}}(t_1)dt_1\widehat{\widetilde{\rho}}(t_0)\int_{t_0}^{t_0+\Delta t} \widehat{\widetilde{R}}(t_1)\widehat{\widetilde{S}}(t_1)dt_1 \\ &- \int_{t_0}^{t_0+\Delta t} dt_1 \int_{t_0}^{t_1} dt_2 \left(\widehat{\widetilde{S}}(t_1)\widehat{\widetilde{R}}(t_1)\right)\left(\widehat{\widetilde{S}}(t_2)\widehat{\widetilde{R}}(t_2)\right)\widehat{\widetilde{\rho}}(t_0) \\ &- \widehat{\widetilde{\rho}}(t_0)\int_{t_0}^{t_0+\Delta t} dt_1 \int_{t_0}^{t_1} dt_2 \widehat{\widetilde{R}}(t_2)\widehat{\widetilde{S}}(t_2)\widehat{\widetilde{R}}(t_1)\widehat{\widetilde{S}}(t_1)\end{aligned} \tag{3.2.21}$$

To move forward, we make additional assumptions. First, we use the Born approximation, assuming that, at any moment in time, the reservoir density matrix does not change with time. Physically, this approximation means that the reservoir is so large that interaction with the system cannot change its temperature. Second, we assume that the reservoir is in thermal equilibrium with the temperature T, i.e., the probability of having the energy E_R is proportional to $\exp(-E_R/T)$ (this assumption is often called the Gibbs ansatz). According to the Gibbs ansatz, in the thermal equilibrium, the reservoir density matrix $\hat{\rho}_R^{th}$ has the form:

$$\hat{\rho}_R(0) = \hat{\rho}_R^{th} = \frac{\exp\left(-\hat{H}_R/T\right)}{Tr\left[\exp\left(-\hat{H}_R/T\right)\right]}.$$

Thus, in the Born approximation, $\widehat{\widetilde{\rho}}(t) = \hat{\rho}_S(t)\hat{\rho}_R^{th}$. Then, the operators $\widehat{\widetilde{\rho}}_1(t_0+\Delta t)$ and $\widehat{\widetilde{\rho}}_2(t_0+\Delta t)$ from Eqs. (3.2.20)–(3.2.21) can be written in the form:

$$\widehat{\widetilde{\rho}}_1(t_0+\Delta t) = i\int_{t_0}^{t_0+\Delta t} dt_1 \hat{\rho}_S(t_0)\widehat{\widetilde{S}}(t_1)\left(\hat{\rho}_R^{th}\widehat{\widetilde{R}}(t_1)\right) - i\int_{t_0}^{t_0+\Delta t} dt_1 \widehat{\widetilde{S}}(t_1)\hat{\rho}_S(t_0)\left(\widehat{\widetilde{R}}(t_1)\hat{\rho}_R^{th}\right) \tag{3.2.22}$$

$$\begin{aligned}\widehat{\widetilde{\rho}}_2(t_0+\Delta t) = &\int_{t_0}^{t_0+\Delta t} dt_1 \int_{t_0}^{t_0+\Delta t} dt_2 \left(\widehat{\widetilde{S}}(t_1)\hat{\rho}_S(t_0)\widehat{\widetilde{S}}(t_2)\right)\left(\widehat{\widetilde{R}}(t_1)\hat{\rho}_R^{th}\widehat{\widetilde{R}}(t_2)\right) \\ &- \int_{t_0}^{t_0+\Delta t}\int_{t_0}^{t_1} dt_2 dt_1 \left(\widehat{\widetilde{S}}(t_1)\widehat{\widetilde{S}}(t_2)\hat{\rho}_S(t_0)\right)\left(\widehat{\widetilde{R}}(t_1)\widehat{\widetilde{R}}(t_2)\hat{\rho}_R^{th}\right) \\ &- \int_{t_0}^{t_0+\Delta t}\int_{t_0}^{t_1} dt_2 dt_1 \left(\hat{\rho}_S(t_0)\widehat{\widetilde{S}}(t_2)\widehat{\widetilde{S}}(t_1)\right)\left(\hat{\rho}_R^{th}\widehat{\widetilde{R}}(t_2)\widehat{\widetilde{R}}(t_1)\right).\end{aligned} \tag{3.2.23}$$

To obtain the density matrix $\widehat{\widetilde{\rho}}_S(t)$ of the system S, we should take the trace of Eq. (3.2.19) over the reservoir operators:

$$\widehat{\widetilde{\rho}}_s(t_0+\Delta t)=Tr_R\widehat{\widetilde{\rho}}(t_0+\Delta t)=Tr_R\widehat{\widetilde{\rho}}(t_0)+\kappa Tr_R\widehat{\widetilde{\rho}}_1(t_0+\Delta t)+\kappa^2 Tr_R\widehat{\widetilde{\rho}}_2(t_0+\Delta t), \tag{3.2.24}$$

In Eq. (3.2.24), similar to Eqs. (3.2.22) and (3.2.23), there appear factors like

$$Tr_R\hat{\rho}_S(t_0)\hat{\rho}_R^{th}\widehat{\widetilde{S}}(t_1)\widehat{\widetilde{R}}(t_1)=\hat{\rho}_S(t_0)\widehat{\widetilde{S}}(t_1)Tr_R\hat{\rho}_R^{th}\widehat{\widetilde{R}}(t_1),$$

which for many physically important reservoir types are equal to zero because the condition $Tr_R\left(\hat{\rho}_R^{th}\widehat{\widetilde{R}}(t_1)\right)=0$ is satisfied [19] (see Problem 1.7).

As follows from Eq. (3.2.22), if $Tr_R\left(\hat{\rho}_R^{th}\widehat{\widetilde{R}}(t_1)\right)=0$, then $Tr_R\widehat{\widetilde{\rho}}_1(t_0+\Delta t)=0$, and in Eq. (3.2.24), only the second-order term in κ remains.

To calculate the time integrals in $\widehat{\widetilde{\rho}}_2(t)$ (see Eq. (3.2.23)), we need to know an explicit expression for $\widehat{\widetilde{S}}(t)$. It can be obtained explicitly only if the eigenstates of the system Hamiltonian $\hat{H}_S$ are known. Otherwise, the described procedure does not work, and other methods for calculating of $\widehat{\widetilde{S}}(t)$ should be used [20].

If we know the eigenstates $|k\rangle$ of the Hamiltonian $\hat{H}_S$, we can expand the operator $\hat{S}$ over the basis by using the equality $\exp\left(i\hat{H}_S t\right)|k\rangle=\exp(i\omega_k t)|k\rangle$. The eigenstates $|k\rangle$ comprise a complete basis in the corresponding Hilbert space, while the transition operators

$$\hat{S}_{k'k''}=|k'\rangle\langle k''| \tag{3.2.25}$$

form the basis for operators in this Hilbert space. The $\hat{S}_{k'k''}=|k'\rangle\langle k''|$ operators are the generalization of σ operators (2.2.6) introduced for the TLS Hilbert space. The expansion of the operator $\hat{S}$ in basis (3.2.25) is

$$\hat{S}=\left[\sum\nolimits_{k'}|k'\rangle\langle k'|\right]S\left[\sum\nolimits_{k''}|k''\rangle\langle k''|\right]=\sum_{k',k''}\langle k'|\hat{S}|k''\rangle\hat{S}_{k'k''}.$$

The quantities $\langle k'|\hat{S}|k''\rangle$ are the matrix element of the operator $\hat{S}$ of Eq. (3.2.7). In the interaction picture, the operator $\hat{S}$ takes the form:

$$\widehat{\widetilde{S}}(t)=\exp\left(i\hat{H}_S t/\hbar\right)\hat{S}\exp\left(-i\hat{H}_S t/\hbar\right)=\sum_{k'k''}\exp(i\Delta\omega_{k'k''}t)\langle k'|\hat{S}|k''\rangle\hat{S}_{k'k''}, \tag{3.2.26}$$

where the summation is performed over $\Delta\omega_{k'k''}=\omega_{k'}-\omega_{k''}$.

On the right-hand side of Eq. (3.2.26), only the exponential factors are time-dependent. This allows us to calculate integrals in Eqs. (3.2.22) and (3.2.23). According to Eq. (3.2.8), $(\Delta\omega_S)^{-1} < \Delta t < 1/\kappa$; therefore, this integration plays the role of time averaging over fast oscillations. This is the key moment in the procedure of eliminating the reservoir variables, allowing us to obtain the explicit time dependence $\widehat{\widetilde{S}}(t)$.

To avoid repetitions, we only discuss the procedure for evaluating the first term in Eq. (3.2.23). After substituting Eq. (3.2.26) into Eq. (3.2.23), we arrive at the integral:

$$\begin{aligned}
&\frac{\kappa^2}{\Delta t}\int_0^{t_0+\Delta t} dt_1 \int_{t_0}^{t_0+\Delta t} dt_2 \left(\widehat{\widetilde{S}}(t_1)\hat{\rho}_S(t_0)\widehat{\widetilde{S}}(t_2)\right) Tr_R\left(\widehat{\widetilde{R}}(t_1)\hat{\rho}_R^{th}\widehat{\widetilde{R}}(t_2)\right) \\
&\quad = \frac{\kappa^2}{\Delta t}\sum_{k'k''k'''k''''} \int_{t_0}^{t_0+\Delta t}\int_{t_0}^{t_0+\Delta t} dt_1 dt_2 \Big[\hat{S}_{k'k''}\widehat{\widetilde{\rho}}_S(t_0)\hat{S}_{k'''k''''} \exp\big(i\big(\Delta\omega_{k'k''}t_1 + \Delta\omega_{k'''k''''}t_2\big)\big) \\
&\qquad \times Tr_R\left(\widehat{\widetilde{R}}(t_2)\widehat{\widetilde{R}}(t_1)\hat{\rho}_R\right)\Big] \\
&\quad = \frac{\kappa^2}{\Delta t}\sum_{k'k''k'''k''''} \hat{S}_{k'k''}\widehat{\widetilde{\rho}}_S(t_0)\hat{S}_{k'''k''''} \int_{t_0}^{t_0+\Delta t} dt_1 \exp\big(i\big(\Delta\omega_{k'k''} + \Delta\omega_{k'''k''''}\big)t_1\big) \\
&\qquad \times \int_{t_0-t_1}^{t_0+\Delta t-t_1} d\tau \exp\big(i\Delta\omega_{k'''k''''}\tau\big)K(\tau).
\end{aligned} \tag{3.2.27}$$

The function $K(t_1 - t_2) = Tr_R\left(\widehat{\widetilde{R}}(t_2)\widehat{\widetilde{R}}(t_1)\hat{\rho}_R\right)$ characterizes the correlation of the reservoir variables over times t_1 and t_2. Below, it is referred to as the reservoir correlation function. The function changes over time with a characteristic scale τ_R. The time τ_R can be roughly estimated as $\hbar/k_BT \sim 10^{-14} s$ [21], where T is the reservoir temperature. In our case, $\tau_R \sim 1/\Delta\omega_S$, where $\Delta\omega_S = \min_{k\neq k'} \Delta\omega_{kk'}$ is the minimum frequency interval between different nondegenerate states.

To calculate time integrals in Eq. (3.2.27), we note that only oscillatory exponents are present in the integrand. Also, since we chose the time interval Δt in such a way that it greatly exceeds all the characteristic times of the system, $1/\Delta\omega_S \ll \Delta t$. Therefore, in Eq. (3.2.27), the integration limits can be extended to infinity. As a result, we can calculate the integrals in Eq. (3.2.27) as

$$\begin{aligned}
&\int_{t_0-t_1}^{t_0+\Delta t-t_1} d\tau\kappa^2 \exp\big(i\Delta\omega_{k'''k''''}\tau\big)K(\tau) \approx \int_{-\infty}^{\infty} \kappa^2 \exp\big(i\Delta\omega_{k'''k''''}\tau\big)K(\tau)d\tau \\
&\quad \equiv \kappa^2 f\big(\Delta\omega_{k'''k''''}\big),
\end{aligned} \tag{3.2.28}$$

where $f(\omega)$ is the Fourier spectrum of the reservoir correlation function $K(\tau)$.

In addition, we suppose that

$$\int_{t_0}^{t_0+\Delta t} dt_1 \exp\left(i\left(\Delta\omega_{k'k''} + \Delta\omega_{k'''k''''}\right)t_1\right) \approx \Delta t \delta_{\Delta\omega_{k'k''},\,-\Delta\omega_{k'''k''''}}, \tag{3.2.29}$$

where $\delta_{\Delta\omega_{k'k''},\,-\Delta\omega_{k'''k''''}}$ is the Kronecker delta. Below, when employing Eqs. (3.2.28) and (3.2.29), we use the notation:

$$\gamma_{k'k''}/2 = \kappa^2 f(\Delta\omega_{k'k''})\left|\langle k'|\hat{S}|k''\rangle\right|^2 \tag{3.2.30}$$

Equation (3.2.29) leads to an important result: in sum (3.2.27), only terms with $\Delta\omega_{k'k''} = -\Delta\omega_{k'''k''''}$ remain. Now, the summation in Eq. (3.2.27) is performed over all possible frequency differences $\omega_{k'k''}$.

We substitute Eq. (3.2.27) into Eq. (3.2.23) and then into Eq. (3.2.19). This gives:

$$\frac{\widehat{\widetilde{\rho}}(t_0+\Delta t) - \widehat{\widetilde{\rho}}(t_0)}{\Delta t} = \sum_{\Delta\omega_{k'k''}} \frac{\gamma_{k'k''}}{2}\left(\left[\hat{S}_{k'k''}, \widehat{\widetilde{\rho}}_S(t_0)\hat{S}^{\dagger}_{k'k''}\right] + \left[\hat{S}_{k'k''}\widehat{\widetilde{\rho}}_S(t_0), \hat{S}^{\dagger}_{k'k''}\right]\right). \tag{3.2.31}$$

Note that $\hat{S}_{k'k''}$ are dimensionless quantities and for any fixed t we have:

$$\left\langle\left[\widehat{\widetilde{S}}(t)\widehat{\widetilde{R}}(t), \widehat{\widetilde{\rho}}\right]\right\rangle \sim O(1).$$

The further consideration is valid for systems with high-quality factor ($\gamma_{k'k''} \ll \Delta\omega_S$). For low-$Q$ systems, instead of using the Lindblad equation, one has to use other methods. For high-Q systems, we can choose Δt from the interval $1/\Delta\omega_S \ll \Delta t \ll 1/\gamma_{k'k''}$. Such a choice means that Δt is much smaller than any characteristic time $1/\gamma_{k'k''}$ of the system. Consequently, the difference in the left-hand side of Eq. (3.2.31) can be replaced with the derivative. The obtained equation is called the Lindblad equation for the density matrix $\widehat{\widetilde{\rho}}_S$ of the system:

$$\frac{\partial\widehat{\widetilde{\rho}}_S(t)}{\partial t} = \sum\nolimits_{\Delta\omega_{k'k''}} \frac{\gamma_{k'k''}}{2}\left(\left[\hat{S}_{k'k''}, \widehat{\widetilde{\rho}}_S(t)\hat{S}^{\dagger}_{k'k''}\right] + \left[\hat{S}_{k'k''}\widehat{\widetilde{\rho}}_S(t), \hat{S}^{\dagger}_{k'k''}\right]\right). \tag{3.2.32}$$

Equation (3.2.32) is obtained under the assumption that $\Delta t \gg 1/\Delta\omega_S$. Thus, employing the Lindblad equation, we have to check that the inequality

$$1/\Delta\omega_S \ll \Delta t \ll 1/\gamma_{k'k''} \sim 1/\left(\kappa^2 f(\Delta\omega_{k'k''})\left|\langle k'|\hat{S}|k''\rangle\right|^2\right)$$

is satisfied. The right-hand side of Eq. (3.2.32) defines the Lindblad superoperator $\hat{L}\left[\widehat{\widetilde{\rho}}_S(t)\right]$. One can show that if the reservoir is in thermal equilibrium with temperature T (so that $\rho_R = \exp(-H_R/T)/Tr(\exp(-H_R/T))$), then the function $\gamma_{kk'}$ satisfies the Kubo-Martin-Schwinger relation [13, 22, 23]:

$$\gamma_{k'k''}/\gamma_{k''k'} = \exp(\hbar\Delta\omega_{k'k''}/kT) \tag{3.2.33}$$

where T is the reservoir temperature (see Problem 1.8).

The integration procedure in Eqs. (3.2.28) and (3.2.29) requires that the integration time Δt be greater than the characteristic inverse frequency $1/\Delta\omega_S$ of the system, $\Delta t \gg 1/\Delta\omega_S$. However, the integration time Δt should not be too large so that expansion (3.2.15) for the evolution operator holds. From Eqs. (3.2.31) and (3.2.32), we can see that the latter requires that the condition $\gamma_{k'k''}\Delta t \ll 1$ must be satisfied. Thus, the criteria for the applicability of the described procedure for eliminating the reservoir variables are the conditions $\gamma_{k'k''} \ll \Delta\omega_S$ and $1/\Delta\omega_S \ll \Delta t \ll 1/\gamma_{k'k''}$.

Having the density matrix in the interaction picture, we can obtain $\hat{\rho}_S(t)$ in the Schrödinger picture by the inverse conversion of $\widehat{\widetilde{\rho}}_S(t)$:

$$\hat{\rho}_S(t) = \exp\left(-i\hat{H}_S t/\hbar\right)\widehat{\widetilde{\rho}}_S(t)\exp\left(i\hat{H}_S t/\hbar\right), \tag{3.2.34}$$

Differentiating this equation with respect to time, we obtain:

$$\frac{\partial\hat{\rho}_S(t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_S, \hat{\rho}_S\right] + \exp\left(-i\hat{H}_S t/\hbar\right)\frac{\partial\widehat{\widetilde{\rho}}_S(t)}{\partial t}\exp\left(i\hat{H}_S t/\hbar\right).$$

Taking into account that $\exp\left(-i\hat{H}_S t/\hbar\right)\widehat{\widetilde{A}}\widehat{\widetilde{B}}\widehat{\widetilde{C}}\exp\left(i\hat{H}_S t/\hbar\right) = \hat{A}\hat{B}\hat{C}$, we obtain that.

$$\begin{aligned}
&\exp\left(-i\hat{H}_S t/\hbar\right)\frac{\partial\widehat{\widetilde{\rho}}_S(t)}{\partial t}\exp\left(i\hat{H}_S t/\hbar\right) \\
&\quad = \exp\left(-i\hat{H}_S t/\hbar\right)\sum\nolimits_{\Delta\omega_{k'k''}}\frac{\gamma_{k'k''}}{2}\left(\left[\hat{S}_{k'k''}, \widehat{\widetilde{\rho}}_S(t)\hat{S}^{\dagger}_{k'k''}\right] + \left[\hat{S}_{k'k''}\widehat{\widetilde{\rho}}_S(t), \hat{S}^{\dagger}_{k'k''}\right]\right)\exp\left(i\hat{H}_S t/\hbar\right) \\
&\quad = \sum\nolimits_{\Delta\omega_{k'k''}}\frac{\gamma_{k'k''}}{2}\left(\left[S_{k'k''}, \hat{\rho}_S(t)S^{\dagger}_{k'k''}\right] + \left[S_{k'k''}\hat{\rho}_S(t), S^{\dagger}_{k'k''}\right]\right)
\end{aligned}$$

And finally, we obtain the Lindblad equation in the Schrödinger picture:

$$\begin{aligned}
\frac{\partial\hat{\rho}_S(t)}{\partial t} &= -\frac{i}{\hbar}\left[\hat{H}_S, \hat{\rho}_S\right] + \sum\nolimits_{\Delta\omega_{k'k''}}\frac{\gamma_{k'k''}}{2}\left(\left[\hat{S}_{k'k''}, \hat{\rho}_S(t)\hat{S}^{\dagger}_{k'k''}\right] + \left[\hat{S}_{k'k''}\hat{\rho}_S(t), \hat{S}^{\dagger}_{k'k''}\right]\right) \\
&\equiv \hat{L}[\hat{\rho}_S(t)].
\end{aligned} \tag{3.2.35}$$

3.2.3 Lindblad Master Equation as a System of the Rate Equations

Lindblad equation (3.2.32) takes a simpler form in the basis of eigenstates $\{|k\rangle\}$ of $\hat{H}_S$. In this basis, the Lindblad equation can be reduced to a system of rate equations.

To show this, we expand both the density matrix:

$$\hat{\rho} = \sum_{|i\rangle|f\rangle \in \{|k\rangle\}} \rho_S^{(i,f)} |i\rangle\langle f|, \tag{3.2.36}$$

and the Hamiltonian $\hat{H}_S$

$$\hat{H}_S = \sum_k \hbar\omega_k |k\rangle\langle k| \tag{3.2.37}$$

over the basis $\{|k\rangle\}$. $\rho_S^{(i,f)}$ is a matrix element of the operator $\hat{\rho}$ between $\hat{H}_S$ eigenstates states $|i\rangle$, $|f\rangle \in \{|k\rangle\}$: $\rho_S^{(i,f)} = \langle i|\hat{\rho}|f\rangle$. Taking into account that $\hat{S}_{if} = |i\rangle\langle f|$ (see Eq. (3.2.25)), we substitute expansions (3.2.36) into Eq. (3.2.32) and equate coefficients at the same $|i\rangle\langle f|$ on the left- and right-hand sides. After some algebra, we obtain [24]:

$$\frac{d\rho_S^{(ii)}}{dt} = \sum_f \gamma_{fi}\rho_S^{(ff)} - \sum_f \gamma_{if}\rho_S^{(ii)}. \tag{3.2.38}$$

$$\frac{d\rho_S^{(if)}}{dt} = -i(\omega_i - \omega_f)\rho_S^{(if)} - \left[\frac{1}{2}\sum_k (\gamma_{ki} + \gamma_{kf})\right]\rho_S^{(if)}, i \neq f. \tag{3.2.39}$$

Equation (3.2.38) describes the dynamics of the diagonal elements of the density matrix. The time derivative of $\rho_S^{(ii)}$ is determined by two terms. The first is responsible for an increase in the $\rho_S^{(ii)}$ due to the transitions from the state $|f\rangle$ to the state $|i\rangle$ with the rate γ_{fi}. The second term describes a decrease in $\rho_S^{(ii)}$ due to the transitions from the state $|i\rangle$ to the state $|f\rangle$ with the rate γ_{if}. After summation over i, one can see that the trace of the density matrix is conserved:

$$\begin{aligned} \sum_i d\rho_S^{(ii)}/dt &= \sum_{if} \gamma_{fi}\rho_S^{(ff)} - \sum_{if} \gamma_{if}\rho_S^{(ii)} = \\ &= \sum_{if} \gamma_{fi}\rho_S^{(ff)} - \sum_{if} \gamma_{fi}\rho_S^{(ff)} 0 = 0 \end{aligned} \tag{3.2.40}$$

In this form, Eq. (3.2.38) is similar to the rate equations commonly used in quantum kinetics (see Refs. [25, 26] and Remark 3.2).

Remark 3.2 **Rate equation.** The approach of the rate equation is often used to describe laser dynamics. In relation to the TLS model of an atom, such an approach is developed based on the simple notion that there should be a balance between the number of atoms undergoing transitions from the ground (excited) to the excited (ground) state and the change in the number of photons being annihilated or created. The simplest mathematical equation describing this process is the rate equation, which relates the time derivative of the photon numbers to the imbalance of the transitions. In our case, it is important that when one photon is absorbed or emitted, the total population of the levels remains unchanged.

Equation (3.2.39) describes the dynamics of the off-diagonal elements of the density matrix. One can see that each off-diagonal element evolves independently from the other density matrix elements. Thus, each off-diagonal element oscillates with the frequency $\omega_i - \omega_f$ and decays exponentially with the rate:

$$\gamma_\sigma = \frac{1}{2}\sum_k \left(\gamma_{ki} + \gamma_{kf}\right). \tag{3.2.41}$$

The quantities $\gamma_{kk'}$ have the meaning of the transition rates between the system eigenstates. Note that, according to Eq. (3.2.30), $\gamma_{kk'}$ depends not only on the density of states of the reservoir $f(\omega)$ but also on the matrix elements $\langle k'|\hat{S}|k\rangle$. If these matrix elements change, e.g., due to changing system eigenstates, the transition rate $\gamma_{kk'}$ also changes even when the reservoirs remain the same. This fact plays an important role in considering Rayleigh scattering in Chap. 6.

To illustrate the application of the apparatus of the density matrix, in the next subsection, we consider a well-known result of spontaneous emission of an excited atom into the reservoir of free space modes (see also Sect. 3.1.)

3.2.4 *Transverse and Longitudinal Decay Times at Spontaneous Emission of an Excited Atom into the Reservoir of Free Space Modes*

To see how the master equation works, we use Eq. (3.2.35) to reproduce the description of the spontaneous emission process of an atom into the reservoir of the free space modes. In Sect. 2.1, this process was considered by employing the Weiskopf-Wigner theory.

Radiation into free space. We start with TLS Hamiltonians (2.2.11) and the reservoir of free space modes (3.1.1). We use the interaction Hamiltonian in the dipole approximation:

$$\hat{H}_{SR} = -\hat{\mathbf{d}} \cdot \mathbf{E} = \sum_{\alpha,\,\mathbf{k}} \sqrt{\frac{2\pi\hbar\omega_{a,\mathbf{k}}}{V}} \mathbf{e}_{\alpha,\mathbf{k}} \cdot \mathbf{d}_{eg} \left(\hat{\sigma} + \hat{\sigma}^{\dagger}\right) = \hbar\Omega_a(\omega_\sigma)\hat{S}\hat{R}, \tag{3.2.42}$$

where $\hat{S} = \left(\hat{\sigma} + \hat{\sigma}^{\dagger}\right)$, $\kappa = \Omega_a(\omega_\sigma)$, and $\Omega_a(\omega_\sigma) = \sqrt{2\pi\omega_\sigma/\hbar V}\left|\mathbf{d}_{eg}\right|$ is the Rabi constant of the interaction taken at the atomic transition frequency ω_σ, and

$$\hat{R} = \frac{1}{\Omega_a(\omega_\sigma)} \sum_{\mathbf{k}} \sqrt{\frac{2\pi\omega_{a,\mathbf{k}}}{\hbar V}} \left(\hat{a}_{\mathbf{k}}^{\dagger} + \hat{a}_{\mathbf{k}}\right).$$

where V is the mode volume. The frequency $\omega_{a,\,\mathbf{k}}$ is the eigenfrequency of the free space mode with the wave vector $\mathbf{k}$ (see Eq. (3.2.30)). For simplicity, we assume that the dipole polarization of the atom is of spherical symmetry. Under this assumption, the polarization of the electric field in the free space mode is immaterial, and we can ignore the vector character of $\mathbf{d}_{eg}$, writing $\mathbf{e}_{\mathbf{k}} \cdot \mathbf{d}_{eg} = d_{eg}$, as we did in Sect. 2.4.

In interaction Hamiltonian (3.2.42), the system is represented by the operator $\hat{S} = \left(\hat{\sigma} + \hat{\sigma}^{\dagger}\right)$. In the interaction picture, this operator has the form (see Eq. (3.2.26)):

$$\begin{aligned}
\widehat{\widetilde{S}}(t) &= \sum_{k'=g}^{e} \sum_{k''=g}^{e} \langle k'|\hat{S}|k''\rangle \exp(i\Delta\omega_{k'k''}t)|k'\rangle\langle k''| \\
&\equiv \langle e|\hat{\sigma}|e\rangle|e\rangle\langle e| + \langle g|\hat{\sigma}|g\rangle|g\rangle\langle g| \\
&\quad + \langle e|\hat{\sigma}|g\rangle \exp\left(i\left(\omega_e - \omega_g\right)t\right)|e\rangle\langle g| + \langle g|\hat{\sigma}|e\rangle \exp\left(i\left(\omega_g - \omega_e\right)t\right)|g\rangle\langle e| \\
&\quad + \langle e|\hat{\sigma}^{\dagger}|e\rangle|e\rangle\langle e| + \langle g|\hat{\sigma}^{\dagger}|g\rangle|g\rangle\langle g| \\
&\quad + \langle e|\hat{\sigma}^{\dagger}|g\rangle \exp\left(i\left(\omega_e - \omega_g\right)t\right)|e\rangle\langle g| + \langle e|\hat{\sigma}^{\dagger}|g\rangle \exp\left(-i\left(\omega_g - \omega_e\right)t\right)|g\rangle\langle e| \\
&= \exp\left(i\left(\omega_g - \omega_e\right)t\right)|g\rangle\langle e| + \exp\left(i\left(\omega_e - \omega_g\right)t\right)|e\rangle\langle g|,
\end{aligned} \tag{3.2.43}$$

where we use the matrix elements of operators $\hat{\sigma}$ and $\hat{\sigma}^{\dagger}$ (see Eq. (2.2.4)). Further, using $\omega_e - \omega_g = \omega_\sigma$, $|e\rangle\langle g| = \hat{\sigma}^{\dagger}$, and $|g\rangle\langle e| = \hat{\sigma}$ (see Eq. (2.2.5), we obtain:

$$\widehat{\widetilde{S}}(t) = \exp(-i\omega_\sigma t)\hat{\sigma} + \exp(i\omega_\sigma t)\hat{\sigma}^{\dagger} \tag{3.2.44}$$

Thus, from the general form of the master equation in the interaction picture (Eq. (3.2.32)), for the TLS, we obtain:

$$\begin{aligned}\frac{\partial\widehat{\widehat{\rho}}_S(t)}{\partial t} &= \frac{\gamma_{eg}}{2}\left(\left[\hat{S}_{eg},\widehat{\widehat{\rho}}_S(t)\hat{S}^\dagger_{eg}\right]+\left[\hat{S}_{eg}\widehat{\widehat{\rho}}_S(t),\hat{S}^\dagger_{eg}\right]\right)+\frac{\gamma_{ge}}{2}\left(\left[\hat{S}_{ge},\widehat{\widehat{\rho}}_S(t)\hat{S}^\dagger_{ge}\right]+\left[\hat{S}_{ge}\widehat{\widehat{\rho}}_S(t),\hat{S}^\dagger_{ge}\right]\right)\\ &= \frac{\gamma_{eg}}{2}\left(\left[\hat{\sigma}^\dagger,\widehat{\widehat{\rho}}_S(t)\hat{\sigma}\right]+\left[\hat{\sigma}^\dagger\widehat{\widehat{\rho}}_S(t),\hat{\sigma}\right]\right)+\frac{\gamma_{ge}}{2}\left(\left[\hat{\sigma},\widehat{\widehat{\rho}}_S(t)\hat{\sigma}^\dagger_{ge}\right]+\left[\hat{\sigma}_{ge}\widehat{\widehat{\rho}}_S(t),\hat{\sigma}^\dagger_{ge}\right]\right)\\ &= \frac{\gamma_{eg}}{2}\left(2\hat{\sigma}^\dagger\widehat{\widehat{\rho}}_S(t)\hat{\sigma}-\hat{\sigma}\hat{\sigma}^\dagger\widehat{\widehat{\rho}}_S(t)-\widehat{\widehat{\rho}}_S(t)\hat{\sigma}\hat{\sigma}^\dagger\right)\\ &\quad+\frac{\gamma_{ge}}{2}\left(2\hat{\sigma}\widehat{\widehat{\rho}}_S(t)\hat{\sigma}^\dagger-\hat{\sigma}^\dagger\hat{\sigma}\widehat{\widehat{\rho}}_S(t)-\widehat{\widehat{\rho}}_S(t)\hat{\sigma}^\dagger\hat{\sigma}\right)\end{aligned} \tag{3.2.45}$$

Here $\gamma_{eg}=2\kappa^2 f(\omega_\sigma)\left|\langle e|\hat{\sigma}^\dagger|g\rangle\right|^2$ and $\gamma_{ge}=2\kappa^2 f(-\omega_\sigma)|\langle g|\hat{\sigma}|e\rangle|^2$ are transition rates from the state $|g\rangle$ to the state $|e\rangle$, and vice versa (see Eq. (3.2.30)). These rates satisfy Kubo-Martin-Schwinger condition (Eq. (3.2.33)), i.e., $\gamma_{ge}=\gamma_{eg}\exp(-\hbar\omega_\sigma/kT)$. We are interested in optical frequencies, $\hbar\omega_\sigma$~2eV, and room temperature, kT~0.026eV; therefore, $\exp(-\hbar\omega_\sigma/kT)$~$10^{-17}$, and we neglect spontaneous transitions from the ground state to the excited and put $\gamma_{eg}=0$. As a result, Eq. (3.2.45) transforms to

$$\frac{\partial\widehat{\widehat{\rho}}_S(t)}{\partial t}=\gamma_{ge}\left(\hat{\sigma}\widehat{\widehat{\rho}}_S(t)\hat{\sigma}^\dagger-\frac{1}{2}\hat{\sigma}^\dagger\hat{\sigma}\widehat{\widehat{\rho}}_S(t)-\frac{1}{2}\widehat{\widehat{\rho}}_S(t)\hat{\sigma}^\dagger\hat{\sigma}\right). \tag{3.2.46}$$

The rate γ_{ge} has the meaning of the rate of spontaneous relaxation of an initially excited atom into free space; we denote this rate as $\gamma_D^{(rad)}$. Indeed, from Eq. (3.2.30), it follows that $\gamma_{ge}=2\kappa^2 f(-\omega_\sigma)|\langle g|\hat{\sigma}|e\rangle|^2=2\kappa^2 f(-\omega_\sigma)$. Substituting into this expression the correlation function $f(\omega)=(2\pi/3)\Pi(\omega)$ of the reservoir of free space modes (see Eq. (3.1.20), Eq. (6.14) in Problem 1.6, and the discussion following this equation) and the coupling constant $\kappa=\sqrt{2\pi\hbar\omega_\sigma/V}\left|\mathbf{d}_{eg}\right|$, we obtain $\gamma_{eg}=4\omega_\sigma^3\left|\mathbf{d}_{eg}\right|^2/(3\hbar c^3)$ that coincides with $\gamma_D^{(rad)}$ found in the Weisskopf-Wigner theory (see also Sect. 3.1).

The Lindblad equation, including the Hamiltonian part, has the form:

$$\frac{\partial\rho_{TLS}}{\partial t}=-\frac{i}{\hbar}\left[\hat{H}_{TLS},\rho_{TLS}\right]+\gamma_D^{(rad)}\left(\hat{\sigma}\rho_{TLS}\hat{\sigma}^\dagger-\frac{1}{2}\hat{\sigma}^\dagger\hat{\sigma}\rho_{TLS}-\frac{1}{2}\rho_{TLS}\hat{\sigma}^\dagger\hat{\sigma}\right), \tag{3.2.47}$$

Equation (3.2.47) looks particularly simple in the basis of the eigenstates $\{|g\rangle,|e\rangle\}$ of the Hamiltonian $\hat{H}_{TLS}$. In this basis, the density matrix has the form:

$$\hat{\rho}_{TLS}=\rho^{(ee)}|e\rangle\langle e|+\rho^{(eg)}|e\rangle\langle g|+\rho^{(ge)}|g\rangle\langle e|+\rho^{(gg)}|g\rangle\langle g|.$$

Substituting these expressions into Eq. (3.2.47), we obtain the following equations for the diagonal and off-diagonal elements of the density matrix:

$$\begin{aligned}\frac{d\rho^{(ee)}}{dt}&=-\gamma_D^{(rad)}\rho^{(ee)},\\ \frac{d\rho^{(gg)}}{dt}&=\gamma_D^{(rad)}\rho^{(ee)},\end{aligned} \tag{3.2.48}$$

and off-diagonal elements

$$\frac{d\rho^{(ge)}}{dt} = -i\omega_\sigma \rho^{(ge)} - \gamma_D^{(rad)}\rho^{(ge)}/2. \tag{3.2.49}$$

Note that in these equations, the terms responsible for the transition from the ground state are absent due to zero temperature of the reservoir (see also Eqs. (3.2.38)–(3.2.39)).

Usually, for the relaxation rate of the off-diagonal elements, one introduces the notation:

$$\gamma_\sigma = \gamma_D^{(rad)}/2. \tag{3.2.50}$$

Since the expectation value of the dipole moment is $\langle d\rangle \sim d_{ge}\langle\hat{\sigma}\rangle = \rho^{ge}d_{ge}$ (see Eq. (2.3.23), the relaxation time of the dipole moment is equal to γ_σ.

The rate of energy relaxation (relaxation of the diagonal element ρ_{ee}) is often referred to as the rate of longitudinal relaxation. The longitudinal relaxation is characterized by the longitudinal decay time $\tau_\parallel = \tau_1 = 1/\gamma_D^{(rad)}$. The relaxation rate of the dipole moment (relaxation of the off-diagonal elements) is referred to as the rate of the transverse relaxation characterized by the transverse decay time $\tau_\perp \equiv \tau_2 \equiv 1/\gamma_\sigma = 2/\gamma_D^{(rad)}$.

In the dipole approximation, for the interaction between the atom and the reservoir defined by Eq. (3.2.42), we have found that $\gamma_\sigma = \gamma_D^{(rad)}/2$. In classical physics, we see the same relationship because the rate of energy loss is proportional to the time derivative of the square of the dipole moment.

We obtain that $\tau_2 = 2/\gamma_D^{(rad)} > \tau_1 = 1/\gamma_D^{(rad)}$. However, in most situations, e.g., in colloidal quantum dots, dye molecules, and superconducting qubits, $\tau_1 > \tau_2$. To understand the reason for this, we consider another type of interaction between the atom and the reservoir.

Remark 3.3 In both Schrödinger and Heisenberg pictures, we obtain that without a dephasing reservoir, $\gamma_D^{(rad)} = 2\gamma_\sigma$. We can also obtain this relationship by using wave function (2.2.2). Indeed, from the assumption that $dC_e(t)/dt = -\left(\gamma_D^{(rad)}/2\right)C_e(t)$, it follows that $d\left(C_e(t)C_e^*(t)\right)/dt = -2\left(\gamma_D^{(rad)}/2\right)C_e(t)C_e^*(t)$, which shows that $\gamma_D^{(rad)} = 2\gamma_\sigma$. When considering the TLS interaction with a dephasing reservoir, we should transition from the wave function to the density matrix description. In the latter case, the decay rates of diagonal and off-diagonal elements of the density matrix are $\gamma_D^{(rad)}$ and γ_σ, respectively. If there is no dephasing, we have $\gamma_D = 2\gamma_\sigma$ (see Eq. (3.2.50)). In the presence of the dephasing reservoir, we obtain

(continued)

Remark 3.3 (continued)
$\gamma_\sigma = \gamma_D^{(rad)}/2 + \gamma_{deph}$. To identify the cause of the disagreement, we employ the Heisenberg picture, in which the operators $\hat{\sigma}^\dagger$ and $\hat{\sigma}$ decay with the rate γ_σ while the operator $\hat{\sigma}^\dagger\hat{\sigma}$ decays with the rate γ_D (see Sect. 3.2.3). Obtaining $\gamma_D^{(rad)} = 2\gamma_\sigma$, we did not take into account noises and corresponding dissipation terms caused by the dephasing reservoir. When this is done, we arrive at the relation $\gamma_\sigma = \gamma_D^{(rad)}/2 + \gamma_{deph}$. The latter result arises because in the equation for $\langle\hat{\sigma}^\dagger\hat{\sigma}\rangle$, the emerging additional terms like $\hat{F}^\dagger_{deph}(t)\hat{\sigma}$ and terms containing the factor γ_{deph} cancel each other. This cancellation does not occur in the equations for operators $\langle\hat{\sigma}^\dagger\rangle$ and $\langle\hat{\sigma}\rangle$. This leads to an increase in γ_σ: $\gamma_\sigma = \gamma_D^{(rad)}/2 + \gamma_{deph}$ while γ_D remaining unchanged.

The interaction with dephasing reservoir. This interaction only leads to the dephasing or decoherence of the system but does not change the TLS energy. Examples are the broadening of the emission line due to collisions with surrounding gas molecules and the elastic interaction with phonons of the substrate on which tested molecules are deposited. The dephasing rate can exceed the energy dissipation rate by several orders of magnitude ($\tau_2^{deph} \ll \tau_2$) and mainly determines the transverse time τ_2^*, so that $1/\tau_2^* \sim 1/\tau_2^{deph}$ (see Remark 3.3).

Let us consider the reservoir of harmonic oscillators described by creation $\hat{c}_n^{dp\dagger}$ and annihilation $\hat{c}_n^{dp}$ operators:

$$\hat{H}_R = \sum_n \hbar\omega_n^{dp}\hat{c}_n^{dp\dagger}\hat{c}_n^{dp}, \tag{3.2.51}$$

and assume that this reservoir interacts with the TLS via the dephasing Hamiltonian

$$\hat{H}_{SR} = \hbar\hat{\sigma}_z\sum_n \kappa_n\left(\hat{c}_n^{dp\dagger} + \hat{c}_n^{dp}\right) = \hbar\kappa_0\hat{S}\hat{R}, \tag{3.2.52}$$

where $\hat{S} = \hat{\sigma}_z = \hat{D}$ (see Eq. (2.2.4)), $\kappa = \sum_n \kappa_n$, and $\hat{R} = \sum_n \kappa_n\left(\hat{c}_n^{dp\dagger} + \hat{c}_n^{dp}\right)/\sum_n \kappa_n$ are the effective coupling constant and the operator representing the dephasing reservoir in Eq. (3.2.7).

Since Hamiltonian (2.2.10) commutes with $\hat{S} = \hat{\sigma}_z$ and with Hamiltonian (3.2.52), the TLS energy is conserved. Thus, Hamiltonian (3.2.52) describes the elastic scattering of the reservoir excitations on the system. In this case, Eq. (3.2.26) takes the form:

$$\widehat{\widetilde{S}}(t) = \exp\left(i\hat{H}_S t/\hbar\right)\hat{S}\exp\left(-i\hat{H}_S t/\hbar\right) = \sum_{k'k''}\exp(i\Delta\omega_{k'k''}t)\hat{S}_{k'k''} = |e\rangle\langle e| - |g\rangle\langle g| = \hat{\sigma}_z \tag{3.2.53}$$

Note that due to the elasticity of scattering, we have to take into account only $k^{'} = k^{''}$, and in the sum $\sum_{k'k''} \exp(i\Delta\omega_{k'k''}t)\hat{S}_{k'k''}$, all values $\Delta\omega_{k'k''}$ may be put to zero. Thus, $\widehat{\widehat{S}} = \hat{S} = \hat{\sigma}_z$, so we arrive at the last equality in Eq. (3.2.53).

Since $\Delta\omega_{k'k'} = 0$, the transition rate $\gamma_{k'k''}/2 = \lambda^2 f(\Delta\omega_{k'k''})\left|\langle k'|\hat{S}|k''\rangle\right|^2$ becomes dephasing rate $\gamma_{deph} = \kappa^2 f_{deph}(0)$. Finally, Eq. (3.2.32) can be rewritten in the following form:

$$\begin{aligned}\frac{\partial\rho_{TLS}}{\partial t} &= -\frac{i}{\hbar}\left[\hat{H}_{TLS},\rho_{TLS}\right] + \gamma_{deph}\left(\hat{\sigma}_z\rho_{TLS}\hat{\sigma}_z - \frac{1}{2}\hat{\sigma}_z\hat{\sigma}_z\rho_{TLS} - \frac{1}{2}\rho_{TLS}\hat{\sigma}_z\hat{\sigma}_z\right)\\ &= -\frac{i}{\hbar}\left[\hat{H}_{TLS},\rho_{TLS}\right] + \gamma_{deph}(\hat{\sigma}_z\rho_{TLS}\hat{\sigma}_z - \rho_{TLS}).\end{aligned} \tag{3.2.54}$$

Since the operator $\hat{\sigma}_z$ commutes with the Hamiltonian H_{TLS}, the transitions between $\rho^{(ee)}$ and $\rho^{(ff)}$ are absent and $\gamma_{fi} = \gamma_{if} = 0$; then, Eqs. (3.2.38) are reduced to

$$\frac{d\rho^{(ee)}}{dt} = 0, \qquad \frac{d\rho^{(gg)}}{dt} = 0. \tag{3.2.55}$$

This means that the energy of the system remains constant:

$$\langle\sigma_z(t)\rangle = \rho_{ee} - \rho_{gg} = \text{const} = \langle\sigma_z(0)\rangle. \tag{3.2.56}$$

For the off-diagonal elements of the density operator, we obtain:

$$\frac{d\rho_{eg}}{dt} = -i\omega_\sigma\rho_{eg} - \gamma_{deph}\rho_{eg}. \tag{3.2.57}$$

This equation shows that due to the dephasing Hamiltonian, the dipole moment of the TLS $\hat{d} = \text{Tr}\left(d_{eg}\rho_{eg}\left(\hat{\sigma} + \hat{\sigma}^\dagger\right)\right) \sim \text{Re}\langle\sigma\rangle$ decays exponentially:

$$\langle\sigma(t)\rangle = \rho_{eg} = \langle\sigma(0)\rangle\exp\left(\left(-i\omega_\sigma - \gamma_{deph}\right)t\right), \tag{3.2.58}$$

i.e., the connection between the off-diagonal elements of the density matrix disappears, and all interference phenomena also disappear.

The stationary density operator is

$$\rho_S^{st} = \begin{pmatrix}\rho_{ee} & 0\\ 0 & \rho_{gg}\end{pmatrix}. \tag{3.2.59}$$

Thus, the interaction with the dephasing reservoir causes the vanishing of the expectation value of the dipole moment $\hat{d} = \mathrm{Tr}\left(d_{eg}\rho_{eg}\left(\hat{\sigma} + \hat{\sigma}^{\dagger}\right)\right) \sim \mathrm{Re}\langle\sigma\rangle$ (see Eq. (3.2.58)). More precisely, while the energy, which is proportional to the square of the dipole moment, is conserved (Eq. (3.2.56)), the off-diagonal elements of the density matrix vanish. This is why this process is called the dephasing process. Naturally, both types of relaxation are present in real systems, and the dipole moment dissipates with the rate:

$$\gamma_{\sigma} = \gamma_D^{(rad)}/2 + \gamma_{deph}. \tag{3.2.60}$$

The considered dephasing reservoir only contributes to the transverse relaxation rate only (see Eq. (3.2.58)) and does not contribute to the longitudinal relaxations. This happens because dephasing Hamiltonian (3.2.52) commutes with the Hamiltonian of the TLS and conserves energy.

As shown above, in the optical range, the interaction with the reservoir of free space modes leads to energy dissipation and gives the ratio of the times of longitudinal and transverse relaxations equal to 2 (see Eq. (3.2.50)). Since, in a real system, this ratio can reach 10^5 while modeling such systems, it is necessary to use both a reservoir describing energy relaxation and a dephasing reservoir.

3.2.5 *Calculation of the Correlator* $\langle\hat{\boldsymbol{\sigma}}_H(t+\boldsymbol{\tau})\hat{\boldsymbol{\sigma}}_H(t)\rangle$

In this subsection, we demonstrate the application of the Lindblad master equation for calculating the correlator $\langle\hat{\sigma}_H(t+\tau)\hat{\sigma}_H(t)\rangle$. We will use this correlator in Chap. 6 to determine the spectrum of Rayleigh scattering.

In the Schrödinger picture, the correlator $\left\langle\hat{A}_H(t+\tau)\hat{B}_H(t)\right\rangle$ can be expressed via the propagator $\hat{P}_L(t_2;t_1)$ of the Lindblad master equation (see Problem 1.9):

$$\left\langle\hat{A}_H(t+\tau)\hat{B}_H(t)\right\rangle = \mathrm{Tr}_S\left(\hat{A}_S\hat{P}_L(t+\tau;t)\left[\left(\hat{B}_S\hat{P}_L(t;0)[\rho_S(0)]\right)\right]\right).$$

Employing this relation, the desired correlator

$$\left\langle\hat{\sigma}_H^{\dagger}(t+\tau)\hat{\sigma}_H(t)\right\rangle = \mathrm{Tr}_S\left(\hat{\sigma}_{Schr}^{\dagger}\hat{P}_L(t+\tau;t)\left[\left(\hat{\sigma}_{Schr}\hat{P}_L(t;0)[\rho_S(0)]\right)\right]\right), \tag{3.2.61}$$

can be calculated using the following algorithm (see Problem 1.9 and Ref. [21]).

For brevity, for $t_2 > t_1$, we express any solution, $\hat{L}_{sol}(t_2)$ to the Lindblad equation via $\hat{P}_L(t_2;t_1)$:

$$\hat{L}_{sol}(t_2) = \hat{P}_L(t_2;t_1)\left[\hat{L}_{sol}(t_1)\right]. \tag{3.2.62}$$

In particular, for the density matrix, we can write:

$$\hat{\rho}_S(t_2) = \hat{P}_L(t_2; t_1)[\hat{\rho}_S(t_1)].$$

According to the Cauchy-Kovalevskaya [27] theorem, such a propagator exists and is uniquely defined. An explicit formula for this propagator is immaterial to us because the solutions to Eq. (3.2.62) are found by computer simulation of the Lindblad equation with the appropriate initial conditions.

First, we utilize the system density matrix $\rho_S(0)$ to determine $\rho_S(t)$ denoted in Eq. (3.2.61) as $\hat{P}_L(t;0)[\rho_S(0)]$. This is achieved by solving the Lindblad master equation in the time interval from 0 to t (see Sects. 3.2.2 and 3.2.3).

Then, acting on $\rho_S(t)$, found in this step, by the operator $\hat{\sigma}_{Schr}$, we obtain the initial condition to the solution of the next Lindblad equation, which we have to solve in the time interval from t to $t + \tau$. In notation (3.2.62), the solution to this problem looks as

$$\hat{L}_{sol}(t+\tau) = \hat{P}_L(t+\tau; t)\left[\hat{\sigma}_{Schr}\hat{P}_L(t;0)[\rho_S(0)]\right].$$

Practically, the solution to such a problem should be found during the computer simulation of the Lindblad master equation.

Finally, to obtain the required correlator (3.2.61), we only have to act on the solution found by the operator by $\hat{\sigma}^{\dagger}_{Schr}$ and take the trace over the system variables.

The application of the obtained correlator to the TLS problem. Let us illustrate the application of the algorithm for the TLS interacting with a reservoir of free space mode that we consider in Sect. 3.2.4.

The Lindblad master equation for the TLS density matrix (see Eq. (3.2.47)) reduces to the system of eqs. (3.2.48)–(3.2.49). These equations can easily be solved analytically:

$$\begin{aligned} \rho^{(ee)}(t) &= \rho_0^{(ee)} e^{-\gamma_D^{(rad)} t}, \qquad \rho^{(gg)}(t) = \rho_0^{(ee)} + \rho_0^{(gg)} - \rho_0^{(ee)} e^{-\gamma_D^{(rad)} t}, \\ \rho^{(ge)}(t) &= \rho_0^{(ge)} e^{\left(-i\omega_\sigma - \gamma_D^{(rad)}/2\right)t}, \qquad \rho^{(eg)}(t) = \rho_0^{(eg)} e^{\left(i\omega_\sigma - \gamma_D^{(rad)}/2\right)t}, \end{aligned} \tag{3.2.63}$$

where $\rho_0^{(ee)}$, $\rho_0^{(ee)}$, $\rho_0^{(ee)}$, and $\rho_0^{(ee)}$ are initial conditions for the density matrix at $t = 0$. Now, we arrive at the following expression for the density matrix at time t:

$$\hat{\rho}_{TLS}(t) \equiv \hat{P}_L(t)[\hat{\rho}_{TLS}(0)] = \begin{pmatrix} \rho_0^{(ee)} e^{-\gamma_D^{(rad)} t} & \rho_0^{(ge)} e^{\left(-i\omega_\sigma - \gamma_D^{(rad)}/2\right)t} \\ \rho_0^{(eg)} e^{\left(i\omega_\sigma - \gamma_D^{(rad)}/2\right)t} & \rho_0^{(ee)}\left(1 - e^{-\gamma_D^{(rad)} t}\right) + \rho_0^{(gg)} \end{pmatrix} \tag{3.2.64}$$

Further,

$$\hat{\sigma}\hat{\rho}_{TLS}(t) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \rho_0^{(ee)} e^{-\gamma_D^{(rad)} t} & \rho_0^{(ge)} e^{\left(-i\omega_\sigma - \gamma_D^{(rad)}/2\right)t} \\ \rho_0^{(eg)} e^{\left(i\omega_\sigma - \gamma_D^{(rad)}/2\right)t} & \rho_0^{(ee)} + \rho_0^{(gg)} - \rho_0^{(ee)} e^{-\gamma_D^{(rad)} t} \end{pmatrix}$$
$$= \begin{pmatrix} 0 & 0 \\ \rho_0^{(ee)} e^{-\gamma_D^{(rad)} t} & \rho_0^{(ge)} e^{\left(-i\omega_\sigma - \gamma_D^{(rad)}/2\right)t} \end{pmatrix} \tag{3.2.65}$$

Then, we need to solve Lindblad master eq. (3.2.65) with respect to τ:

$$\frac{\partial \widetilde{\rho}_{TLS}(t,\tau)}{\partial \tau} = -\frac{i}{\hbar}\left[\hat{H}_{TLS}, \widetilde{\rho}_{TLS}\right] + \gamma_D^{(rad)}\left(\hat{\sigma}\widetilde{\rho}_{TLS}\hat{\sigma}^\dagger - \frac{1}{2}\hat{\sigma}^\dagger\hat{\sigma}\widetilde{\rho}_{TLS} - \frac{1}{2}\widetilde{\rho}_{TLS}\hat{\sigma}^\dagger\hat{\sigma}\right), \tag{3.2.66}$$

with the initial condition

$$\widetilde{\rho}_{TLS}(t,0) = \begin{pmatrix} 0 & 0 \\ \rho_0^{(ee)} e^{-\gamma_D^{(rad)} t} & \rho_0^{(eg)} e^{\left(i\omega_\sigma - \gamma_D^{(rad)}/2\right)t} \end{pmatrix} \tag{3.2.67}$$

To obtain the solution to Eq. (3.2.66) with initial condition (3.2.67), in the general solution (3.2.64), one has to turn $\rho_0^{(ee)}$ and $\rho_0^{(eg)}$ to zero, $\rho_0^{(ge)}$ to $\rho_0^{(ee)} \exp\left(-\gamma_D^{(rad)} t\right)$, and $\rho_0^{(gg)}$ to $\rho_0^{(eg)} \exp\left(\left(i\omega_\sigma - \gamma_D^{(rad)}/2\right)t\right)$. Then, the solution takes the form:

$$\widetilde{\rho}_{TLS}(t,\tau) = \begin{pmatrix} 0 & 0 \\ \rho^{(ee)}(0) e^{-\gamma_D^{(rad)} t} e^{\left(i\omega_\sigma - \gamma_D^{(rad)}/2\right)\tau} & \rho^{(eg)}(0) e^{\left(i\omega_\sigma - \gamma_D^{(rad)}/2\right)t} \end{pmatrix} \tag{3.2.68}$$

Further, using Eq. (3.2.68), we can find the value $\hat{\sigma}^\dagger\widetilde{\rho}_{TLS}(t,\tau)$:

$$\hat{\sigma}^\dagger\widetilde{\rho}_{TLS}(t,\tau) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 \\ \rho_0^{(ee)} e^{-\gamma_D^{(rad)} t} e^{\left(i\omega_\sigma - \gamma_D^{(rad)}/2\right)\tau} & \rho_0^{(eg)} e^{\left(i\omega_\sigma - \gamma_D^{(rad)}/2\right)t} \end{pmatrix}$$
$$= \begin{pmatrix} \rho_0^{(ee)} e^{-\gamma_D^{(rad)} t} e^{\left(i\omega_\sigma - \gamma_D^{(rad)}/2\right)\tau} & \rho_0^{(eg)} e^{\left(i\omega_\sigma - \gamma_D^{(rad)}/2\right)t} \\ 0 & 0 \end{pmatrix} \tag{3.2.69}$$

and finally

$$\left\langle \hat{\sigma}^\dagger(t+\tau)\hat{\sigma}(t) \right\rangle = Tr\left(\hat{\sigma}^\dagger\widetilde{\rho}_{TLS}(t,\tau)\right) = \rho_0^{(ee)} e^{-\gamma_D^{(rad)} t} e^{\left(i\omega_\sigma - \gamma_D^{(rad)}/2\right)\tau} \tag{3.2.70}$$

3.3 Fermi's Golden Rule

In practice, to quickly obtain an estimate for the probability amplitude for a transition between states, one can resort to Fermi's golden rule. This rule is discussed in almost every textbook on quantum mechanics (see, e.g., Refs. [15, 28–30]) in connection with the transition of a quantum system from a discrete stationary state to a quasi-continuum of states. Besides beta decay, Fermi's golden rule is used in the theory of ionization and spontaneous emission. In most cases, this is a transition from a discrete state to a continuous spectrum state.

Below, we show that Fermi's golden rule can only be derived for transitions in which the final state belongs to the continuous spectrum. Usually, for an atom interacting with a single mode of an EM field, Fermi's golden rule is derived using the standard perturbation theory.

Suppose that the Hamiltonian of the system can be represented in the form $\hat{H}_S = \hat{H}^{(0)} + \hat{V}(t)$, where $\hat{H}^{(0)}$ is the Hamiltonian of an atom and $\hat{V}(t)$ is the perturbation caused by a single mode of the time-dependent classical field. The wave function for this system obeys the Schrödinger equation. We assume that the eigenstates $\left|\psi_i^{(0)}\right\rangle$ of the Hamiltonian $\hat{H}^{(0)}$ are known, and their time dependence is given by $\exp(i\omega_i t)$. The wave function $|\psi(t)\rangle$ can be searched for as a linear combination of the eigenfunctions of the unperturbed Hamiltonian $\hat{H}^{(0)}$:

$$|\psi(t)\rangle = \sum_l a_l(t)\exp(i\omega_l t)\left|\psi_l^{(0)}\right\rangle. \tag{3.3.1}$$

Suppose that at the initial moment, the atom is in the state $|\psi_i\rangle$. It means that $a_i(0) = 1$, while $a_l(0) = 0$ $(l \neq i)$. Since the perturbation $\hat{V}(t)$ is small, $|a_i(t)| \gg |a_l(t)|$, so we can still assume that for $l \neq i$, $a_l(t) = 0$. Therefore,

$$|\psi(t)\rangle = \sum_l a_l(t)\exp(i\omega_l t)\left|\psi_l^{(0)}\right\rangle \approx a_i(t)\exp(i\omega_i t)\left|\psi_i^{(0)}\right\rangle. \tag{3.3.2}$$

This is correct for small t only. According to the first order of the perturbation theory, the probability amplitude, $a_{fi}(t)$, of finding the atom in the final state $\left|\psi_f^{(0)}\right\rangle$ at the time moment t, if at the initial time moment, it is in the initial state $\left|\psi_i^{(0)}\right\rangle$, can be expressed as

$$a_{fi}^{(1)}(t) = -\frac{i}{\hbar}\int_0^t \left\langle \psi_f^{(0)}\middle|\hat{V}(t)\middle|\psi_i^{(0)}\right\rangle \exp\left(i\omega_{fi}\tau\right)d\tau, \tag{3.3.3}$$

where the transition frequency between the initial $|\psi_i\rangle$ and the final $|\psi_f\rangle$ states is denoted as $\omega_{fi} = \omega_f - \omega_i$. In a particular case of a periodic perturbation of the form $\hat{V}\exp(-i\omega_{ext}t)$, we obtain:

$$a_{fd}^{(1)}(t) = -\langle\psi_f|\hat{V}|\psi_i\rangle\frac{\exp\left(i\left(\omega_{fi}-\omega_{ext}\right)t\right)-1}{\hbar\left(\omega_{fi}-\omega_{ext}\right)}, \text{if } \omega_{fd}-\omega_{ext}\neq 0 \tag{3.3.4}$$

and

$$a_{fd}^{(1)}(t) = -\left\langle\psi_f^{(0)}\middle|\hat{V}\middle|\psi_d^{(0)}\right\rangle\frac{t}{\hbar}, \text{if } \omega_{fd}-\omega_{ext}=0. \tag{3.3.5}$$

Equation (3.3.5) shows that in the resonant case, $\omega_{fi} - \omega_{ext} = 0$, the probability amplitude $a_{fi}^{(1)}(t)$ increases linearly with time. The perturbation theory is correct only when $\left|\langle\psi_f|\hat{V}|\psi_i\rangle t\right| \ll 1$; therefore, there is not only a limitation on the magnitude of the external influence but also on the time of observation. In particular, for $t > 1/\left|\langle\psi_f|\hat{V}|\psi_i\rangle t\right|$, we cannot confine ourselves to the first order of the perturbation theory but have to consider higher orders of the perturbation. In this case, we should take into account transitions between other states that lead to complex behavior, which spectrum contains all ω_l. This motion does not have a stationary state with the fixed energy because the Hamiltonian $\hat{H}_S = \hat{H}^{(0)} + \hat{V}(t)$ is time-depended, and the energy is not conserved. In the case of a TLS, for $t > 1/\left|\langle\psi_f|\hat{V}|\psi_i\rangle t\right|$, the system performs Rabi oscillations (see Sect. 2.4 for details).

Taking into account this restriction and limiting ourselves by the first order of the perturbation theory, for the squared probability amplitude, we have:

$$p(t)_{fi}^{(1)} = \left|a_{fi}^{(1)}(t)\right|^2 = \begin{cases} \left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2 t^2/\hbar^2, & \omega_{fi}=\omega_{ext}, \\ \left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2 \dfrac{\sin^2\left(\left(\omega_{fi}-\omega_{ext}\right)t/2\right)}{4\hbar^2\left(\left|\omega_{fi}-\omega_{ext}\right|/2\right)^2}, & \omega_{fd}\neq\omega_{ext}. \end{cases} \tag{3.3.6}$$

We have obtained the probability of finding the system at the moment t in a given state. However, this probability diverges with time: $p(t)_{fi}^{(1)} \sim t^2$; hence, as mentioned above, such an approach is applicable only for short time intervals. Therefore, we cannot consider $p(t)_{fi}^{(1)}$ given by Eq. (3.3.6) as the transition probability.

Below, following the Weisskopf-Wigner approach, we show that replacing the final state of a reservoir with a continuum of states allows one to find a correct solution for the problem.

Usually, one considers an ensemble of systems with slightly different final states in the frequency interval $\Delta\omega_f \ll \omega_f$ [15, 31]. Then, physical quantities should be averaged over this ensemble by using the density of final states $\Pi(\omega_k)$ (see Eq. (3.1.20)).

The meaning of this procedure is that the problem of the electron transition between discrete atomic levels is replaced by the problem of the transition from a discrete state to a continuum of states. Fermi's theory of the transitions to some discrete state with lower energy is close to the Weisskopf-Winer theory, while the transitions with an increase in the eigenenergy Fermi considered ionization [2], e.g., transitions to a reservoir with the continuum of eigenstates. Thus, the ensemble of final states considered here plays the role of a reservoir. Then, instead of Eq. (3.3.6), we obtain:

$$p(t)_{fi}^{(1)} = \int_{\omega_f - \Delta\omega_f/2}^{\omega_f + \Delta\omega_f/2} \left|\langle\psi_k|\hat{V}|\psi_i\rangle\right|^2 \left(\frac{\pi}{4\hbar^2}\right) \frac{\sin^2((\omega_k - \omega_i - \omega_{ext})t/2)}{\pi(|\omega_k - \omega_i - \omega_{ext}|/2)^2} \Pi(\omega_k) d\omega_k \tag{3.3.7}$$

As time increases, for $t \gg 1/\omega_k$ (where ω_k belongs to the interval $\Delta\omega$), the frequency interval, in which the function $\frac{\sin^2((\omega_k - \omega_i - \omega_{ext})t/2)}{\pi(|\omega_k - \omega_i - \omega_{ext}|/2)^2}$ differs from zero significantly, decreases. Therefore, instead of $t \gg 1/\omega_k$, we should use $t \gg 1/\Delta\omega$. Since $\Delta\omega_f \ll \omega_f$ and $\omega_f \sim \omega_i \sim \omega_{ext}$, $\Delta\omega_f \ll \omega_{ext}$. Then, in Eq. (3.3.7), we can use the limit $\lim_{t\to\infty} \frac{\sin^2(\varepsilon t)}{\pi t \varepsilon^2} = \delta(\varepsilon)$. Using $\varepsilon = (\omega_k - \omega_i - \omega_{ext})/2$, we can rewrite Eq. (3.3.7) as

$$\begin{aligned} p(t)_{fi}^{(1)} &= \int_{\omega_f - \Delta\omega_f/2}^{\omega_f + \Delta\omega_f/2} \left|\langle\psi_f|\hat{V}|\psi_i\rangle\right|^2 \left(\frac{\pi t}{4\hbar^2}\right) \delta\big((\omega_f + \omega' - \omega_i - \omega_{ext})/2\big) \Pi(\omega') d\omega' \\ &= t\frac{\pi}{2\hbar^2} \left|V(\omega_{fi})\right|^2 \Pi(\omega_f - \omega_i - \omega_{ext}) \end{aligned} \tag{3.3.8}$$

This equation constitutes Fermi's golden rule. It shows that, even in the first order of the perturbation theory, the probability per unit time $p^{(1)}(t)/t$ to find the system in the final state has a constant value.

Another derivation of Fermi's golden rule is based on considering incident light, the frequency spectrum $F(\omega_{ext})$ of which has a finite line half-width $\Delta\omega_{txt}$. To deal with probabilities instead of amplitudes of probabilities, we should assume that there is no interference between different frequency components and describe such a spectrum with the density of states [32, 33].

Averaging probability (3.3.6) over the spectrum of incident light, we obtain:

$$
\begin{aligned}
p^{(1)}(t)/t &= \frac{\pi}{\hbar^2}\left|\langle\psi_k|\hat{V}|\psi_i\rangle\right|^2 \int \frac{\sin^2((\omega_k-\omega_i-\omega_{ext})t/2)}{\pi\left(\left|\omega_k-\omega_i-\omega_{ext}\right|^2/2\right)t} F(\omega_{ext})d\omega_{ext} \\
&\approx \left(\frac{\pi}{2\hbar^2}\right)\left|\langle\psi_k|\hat{V}|\psi_i\rangle\right|^2 F(\omega_k-\omega_i-\omega_{ext})
\end{aligned}
\tag{3.3.9}
$$

That is identical to Eq. (3.3.8).

This approach can also be used when the final state is a *single* excited state. In this case, we have to take into account that Eq. (3.3.8) is obtained using the perturbation theory. Consequently, it is valid at times smaller than the longitudinal decay time. Thus, the time interval for applying Fermi's golden rule is limited from above by $1/\gamma_D^{(rad)}$. On the other hand, integrating probabilities over the frequency interval in Eqs. (3.3.7) and (3.3.9) means that we disregard all interference phenomena. Such a consideration is reasonable for times greater than the transverse decay time $1/\gamma_\sigma$, in which diagonal elements of the density matrix vanish (see Eq. (3.2.49)).

Thus, our consideration is reasonable at times $1/\gamma_\sigma \ll t \ll 1/\gamma_D^{(rad)}$. Without a dephasing reservoir $\gamma_D^{(rad)} = 2\gamma_\sigma$ [13, 21] and $1/\gamma_\sigma > 1/\gamma_D^{(rad)}$. This is opposite to the former inequality, and therefore, such an approach cannot be used. Fortunately, the dephasing reservoir exists in most experiments [34–38]. The interaction with this reservoir makes $1/\gamma_\sigma \ll 1/\gamma_D$ (see Sect. 3.2). Thus, applying Fermi's golden rule also requires an interaction of a quantum system with some dephasing reservoir of the continuum of modes.

Without such an assumption, we are left with formula (3.3.6), which is the first term in the expansion of the perturbation theory series. However, the complexity of applying Fermi's golden rule to calculating the transition probability is hidden in higher-order terms. If we take into account the interaction with only one mode, then when considering all terms, we obtain the Rabi oscillations. If we account for a reservoir with a continuum of states, formula (3.3.9) becomes valid. If the number of states is countable, then the revival phenomenon can occur, and the system returns to a state in which the contribution of the excited state is of the order of $O(1)$. Moreover, we can lengthen the observation time if the atom interaction with the reservoir does not involve revival. To conclude, regardless of whether an atom absorbs or emits a photon, it should be viewed as an open system interacting with some dephasing reservoir of continuum modes [3, 6, 7].

3.4 Heisenberg-Langevin Equations

In Sect. 2.4, employing the Heisenberg picture, we have considered the dynamics of a closed Hermitian system consisting of a TLS and a single classical EM mode. In the current section, we move further by taking into account the interaction of the system with a free space mode reservoir, described by the Hamiltonian $\hat{H}_E = \sum\limits_{\alpha,\mathbf{k}} \hbar\omega_{a,\mathbf{k}} \hat{a}^+_{\alpha,\mathbf{k}} \hat{a}_{\alpha,\mathbf{k}}$. As in Sect. 3.1, we assume that the reservoir is so large that

it is always in the state of thermal equilibrium (*the Born approximation*). Below, we eliminate the variables of the reservoir of free space modes.

In the Heisenberg picture, the TLS is described by the Hamiltonian (3.1.1) employed in the Weisskopf-Wigner approach to describe spontaneous emission. This implies that the reservoir consists of free space modes only. The Heisenberg equations of motion for atomic and free space field variables have the form:

$$\frac{d\hat{\sigma}_H}{dt} = -i\omega_\sigma \hat{\sigma}_H + i\hat{D}_H \sum_{\mathbf{k}} \Omega_{a,\mathbf{k}} \hat{a}_{\alpha,\mathbf{k}} \tag{3.4.1}$$

$$\frac{d\hat{\sigma}_H^\dagger}{dt} = i\omega_\sigma \hat{\sigma}_H^\dagger - iD_H \sum_{\mathbf{k},\,\alpha} \Omega_{a,\mathbf{k}}^* \hat{a}_{\mathbf{k}}^\dagger \tag{3.4.2}$$

$$\frac{d\hat{D}_H}{dt} = 2i \sum_{\mathbf{k}} \Omega_{a,\mathbf{k}} \left(\hat{a}_{\alpha,\mathbf{k}}^\dagger \hat{\sigma}_H - \hat{\sigma}_H^\dagger \hat{a}_{\alpha,\mathbf{k}} \right) \tag{3.4.3}$$

$$\frac{d\hat{a}_{\mathbf{k}}}{dt} = -i\omega_{a,\mathbf{k}} \hat{a}_{\alpha,\mathbf{k}} - i\Omega_{a,\mathbf{k}} \hat{\sigma}_H \tag{3.4.4}$$

where $\hat{D}_H = 2\hat{\sigma}_H{}^\dagger \sigma_H - \hat{I}$. Integration of Eq. (3.4.4) gives:

$$\hat{a}_{\alpha,\mathbf{k}}(t) = \hat{a}_{\alpha,\mathbf{k}}(0) \exp(-i\omega_{a,\mathbf{k}} t) - i\Omega_{a,\mathbf{k}} \int_0^t d\tau \exp(-i\omega_{a,\mathbf{k}}(t-\tau)) \hat{\sigma}(\tau) \tag{3.4.5}$$

After substituting this result into Eq. (3.4.1), changing the integration variable from τ to $t - \tau$, and making the transition to the slowly varying amplitudes, $\hat{\sigma}_H(t) \to \hat{\sigma}_{H\,slow}(t) \exp(-i\omega_\sigma t)$, we can rewrite Eq. (3.4.1) for the operator $\hat{\sigma}_{H\,slow}(t)$ as

$$\frac{d\hat{\sigma}_{H\,slow}}{dt} = \hat{D}_H(t) \sum_{\alpha,\,\mathbf{k}} |\Omega_{a,\mathbf{k}}|^2 \int_0^t d\tau \exp(-i(\omega_{a,\mathbf{k}} - \omega_\sigma)\tau) \hat{\sigma}_{H\,slow}(t-\tau) + \hat{F}_\sigma(t), \tag{3.4.6}$$

where we introduce the notation.

$$\hat{F}_\sigma(t) = i\hat{D}_H \sum_{\mathbf{k}} \Omega_{a,\mathbf{k}} \hat{a}_{\mathbf{k}}(0) \exp(-i\omega_{a,\mathbf{k}} t) \tag{3.4.7}$$

One can show (Problem 1.10) that the expectation value of operator (3.4.7) is equal to zero, $\langle \hat{F}_\sigma(t) \rangle = 0$, while its correlation function is proportional to the δ-function,

$\left\langle \hat{F}_\sigma^\dagger(t)\hat{F}_\sigma(t')\right\rangle \propto \delta(t-t')$. Thus, $\hat{F}_\sigma(t)$ has the same correlation properties as white noise. For this reason, this term is called the noise term.

In deriving Eq. (3.4.6), we have not yet used any approximations; however, to solve this equation, we should use the Markov approximation described in Sect. 3.1 (see the transition from Eq. (3.1.9) to Eq. (3.1.10)). Using this approximation results in neglecting the system memory and assuming that $\hat{\sigma}_{slow}(t-\tau) \simeq \hat{\sigma}(t)$. This yields:

$$\begin{aligned}\frac{d\hat{\sigma}_{H\,slow}}{dt} &\simeq \hat{D}_H(t)\hat{\sigma}_{H\,slow}(t)\sum_{\mathbf{k}}|\Omega_{a,\mathbf{k}}|^2\int_0^\infty d\tau\exp(-i(\omega_{a,\mathbf{k}}-\omega_\sigma)\tau)+\hat{F}_\sigma(t)\\ &= -\hat{\sigma}_{H\,slow}\sum_{\mathbf{k}}|\Omega_{a,\mathbf{k}}|^2\int_0^\infty d\tau\exp(-i(\omega_{a,\mathbf{k}}-\omega_\sigma)\tau)+\hat{F}_\sigma(t)\end{aligned} \tag{3.4.8}$$

In obtaining this equation, we use the relationship $\hat{D}_H = 2\hat{\sigma}_H{}^\dagger\sigma_H - \hat{I}$ or $\hat{D}_H\hat{\sigma}_{H\,slow} = -\hat{\sigma}_{H\,slow}$.

Finally, using the density of states of free space modes, we can move from the summation over $\mathbf{k}$ to the integration over ω. The integration can be performed analytically using the Sokhotski formula (see Eqs. (3.1.15) and (3.1.16)). In the end, we arrive at

$$\frac{d\hat{\sigma}_{H\,slow}}{dt} = -\gamma_\sigma\hat{\sigma}_{H\,slow}+\hat{F}_\sigma(t), \tag{3.4.9}$$

where

$$\begin{aligned}\gamma_\sigma &= \pi\sum_k|\Omega_{a,\mathbf{k}}|^2\delta(\omega_{a,\mathbf{k}}-\omega_\sigma)\\ &= \pi\int d\omega\Pi(\omega)\Omega_a^2(\omega)\delta(\omega-\omega_\sigma) = \pi\Pi(\omega_\sigma)\Omega_a^2(\omega_\sigma) = \gamma_D^{(rad)}/2.\end{aligned} \tag{3.4.10}$$

In Eq. (3.4.10), the transition from summation to integration reflects the "continuity" of the reservoir spectrum. The last equality is valid since we consider the reservoir of free space modes. This equality coincides with the one obtained in the Schrödinger picture (see Eqs. (3.1.18) and (3.1.21)). In the Schrödinger picture, we deal with the probability amplitude $C_e(t)$, which relaxes with the rate γ_σ, and with the probability $|C_e(t)|^2 = C_e(t)C_e^*(t)$, which relaxes with the rate γ_D, while in the Heisenberg picture, we deal with the operator $\hat{\sigma}_H(t)$, whose relaxation rate is γ_σ, and with the operator of the population inversion $\hat{D}_H = 2\hat{\sigma}_H{}^\dagger\sigma_H - \hat{I}$. In both pictures, the relaxation rate of the product of operators is double of that of each operator. In reality, however, the elastic coupling with the thermal reservoir may lead to the inequality $\gamma_\sigma \gg \gamma_D$ [34–38] (see Remark 3.3).

Thus, we have shown that similar to the Weisskopf-Wigner theory of spontaneous radiation, after the exclusion of the reservoir variables from Eqs. (3.4.9) and (3.4.10), the terms describing the TLS interaction with the reservoir of the infinite

number of modes are transformed into the terms describing dissipation (spontaneous emission) (Eq. (3.4.10)), and noise (Eq. (3.4.7)).

In Eq. (3.4.9), the dissipation term $-\gamma_\sigma \hat{\sigma}_{H\,slow}$ is responsible for the system reaching the stationary state, while the noise term $\hat{F}_\sigma(t)$ determines the correlation of time-fluctuation properties of the state. Both these terms are due to the interactions of the TLS with free space modes. These interactions are described by coupling constants $\Omega_{\mathbf{k},\,\alpha}$, which are directly included in the expressions for noise (Eq. (3.4.7)), and dissipation (Eq. (3.4.10)). The presence of these terms is the manifestation of the fluctuation-dissipation theorem that links the emergence of noise with dissipation and vice versa [6, 39].

Now, we come back to fast-oscillating variables. Performing a similar procedure for Eqs. (3.4.2)–(3.4.3), we arrive at the equations for the operators $\hat{\sigma}_H(t)$, $\hat{\sigma}_H^\dagger(t)$, and $\hat{D}_H$:

$$\frac{d\hat{\sigma}_H}{dt} = (-i\omega_\sigma - \gamma_\sigma)\hat{\sigma}_H + \hat{F}_\sigma(t) \tag{3.4.11}$$

$$\frac{d\hat{\sigma}_H^\dagger}{dt} = (i\omega_\sigma - \gamma_\sigma)\hat{\sigma}_H^\dagger + \hat{F}_{\sigma^\dagger}(t) \tag{3.4.12}$$

$$\frac{d\hat{D}_H}{dt} = -\gamma_D\left(\hat{D}_H - \hat{D}_0\right) + \hat{F}_D(t) \tag{3.4.13}$$

Since we set the reservoir temperature to zero, we should assume $\hat{D}_0 = -\hat{I}$.

Equations (3.4.12) and (3.4.13) are called Heisenberg-Langevin equations. In these equations, the noise terms are obtained similarly to the term $\hat{F}_\sigma(t)$ in Eq. (3.4.7). These terms have the form:

$$\hat{F}_{\sigma^\dagger}(t) = iD_H \sum_{\mathbf{k}} \Omega_{a,\mathbf{k}} \hat{a}_{\mathbf{k}}^\dagger(0) \exp(i\omega_{a,\mathbf{k}} t),$$

$$\hat{F}_D(t) = 2i \sum_{\mathbf{k}} \Omega_{a,\mathbf{k}} \left(\hat{a}_{\mathbf{k}}^\dagger(0) \exp(i\omega_{a,\mathbf{k}} t)\hat{\sigma}_H - \text{h.c.}\right).$$

The correlation properties of these noise terms are considered in Problem 1.10.

We have completed the elimination of the reservoir variables, arriving at the Heisenberg-Langevin eqs. (3.4.11)–(3.4.13), which correctly describe the time evolution of a TLS in the presence of radiation losses.

3.4.1 *Heisenberg Picture of Dynamics of Two-Level System Driven by External Field*

In the previous section, we considered the emission of an excited TLS interacting with a reservoir in the absence of an external field. Now, we take into account the external field. We consider the TLS, the reservoir of free space modes, and the

external field as a closed Hermitian system. For the description of the dipole interaction of the TLS with the modes of the EM field, we employ the rotating wave approximation (see the text above Eq. (2.4.12)). Ultimately, we arrive at the following Hamiltonian:

$$\hat{H} = \hbar\omega_\sigma \hat{\sigma}_H^\dagger \hat{\sigma}_H + \sum_{\mathbf{k}} \hbar\omega_{a,\mathbf{k}} \hat{a}_{\mathbf{k}}^+ \hat{a}_{\mathbf{k}} + \sum_{\alpha,\mathbf{k}} \hbar\Omega_{a,\mathbf{k}} \left(\hat{a}_{\alpha,\mathbf{k}}^+ \hat{\sigma}_H + \hat{a}_{\alpha,\mathbf{k}} \hat{\sigma}_H^\dagger \right) + \hbar\Omega_{ext} \left(\hat{\sigma}_H e^{i\omega_{ext}t} + \hat{\sigma}_H^\dagger e^{-i\omega_{ext}t} \right) \tag{3.4.14}$$

Using this Hamiltonian, one can obtain the system of the Heisenberg equations for the operators $\hat{\sigma}, \hat{\sigma}^\dagger, \hat{D},$ and $\hat{a}_{\alpha,\mathbf{k}}$:

$$\frac{d\hat{\sigma}_H}{dt} = -i\omega_\sigma \hat{\sigma}_H + i\hat{D}_H \sum_{\mathbf{k}} \Omega_{a,\mathbf{k}} \hat{a}_{\alpha,\mathbf{k}} + i\Omega_{ext} \hat{D}_H \exp(-i\omega_{ext}t) \tag{3.4.15}$$

$$\frac{d\hat{\sigma}_H^\dagger}{dt} = i\omega_\sigma \hat{\sigma}_H^\dagger - iD_H \sum_{\mathbf{k}} \Omega_{a,\mathbf{k}} \hat{a}_{\alpha,\mathbf{k}}^\dagger - i\Omega_{ext} \hat{D}_H \exp(-i\omega_{ext}t) \tag{3.4.16}$$

$$\frac{d\hat{D}_H}{dt} = 2i \sum_{\alpha,\mathbf{k}} \Omega_{a,\mathbf{k}} \left(\hat{a}_{\alpha,\mathbf{k}}^\dagger \hat{\sigma}_H - \hat{\sigma}_H^\dagger \hat{a}_{\alpha,\mathbf{k}} \right) + 2i\Omega_{ext} (\hat{\sigma}_H \exp(i\omega_{ext}t) - \hat{\sigma}_H \exp(-i\omega_{ext}t)) \tag{3.4.17}$$

$$\frac{d\hat{a}_{\alpha,\mathbf{k}}}{dt} = -i\omega_{a,\mathbf{k}} \hat{a}_{\alpha,\mathbf{k}} - i\Omega_{a,\mathbf{k}} \hat{\sigma}_H \tag{3.4.18}$$

To obtain the Heisenberg-Langevin equations, we should exclude the reservoir operators $\hat{a}_{\mathbf{k},\alpha}$ (see the beginning of Sect. 3.4). As a result, this yields:

$$\frac{d\hat{\sigma}_H}{dt} = (-i\omega_\sigma - \gamma_\sigma)\hat{\sigma}_H + i\Omega_{ext} \hat{D}_H \exp(-i\omega_{ext}t) + \hat{F}_\sigma(t) \tag{3.4.19}$$

$$\frac{d\hat{\sigma}_H^\dagger}{dt} = (i\omega_\sigma - \gamma_\sigma)\hat{\sigma}_H^\dagger - i\Omega_{ext} \hat{D}_H \exp(i\omega_{ext}t) + \hat{F}_{\sigma^\dagger}(t) \tag{3.4.20}$$

$$\frac{d\hat{D}_H}{dt} = -\gamma_D (\hat{D}_H + \hat{I}) + 2i\Omega_{ext} \left(\hat{\sigma}_H \exp(i\omega_{ext}t) - \hat{\sigma}_H^\dagger \exp(-i\omega_{ext}t) \right) + \hat{F}_D(t) \tag{3.4.21}$$

These equations describe an open system (the TLS and the incident field), which is a part of the closed system described by Hamiltonian (3.4.14). Using these equations, we can describe the effect of light radiation on the atom's dynamical spectrum. In the end, we obtain the spectrum of emitted photons connected with the spectrum of the TLS oscillations [6].

According to the Wiener-Khinchin theorem, the spectrum of the system oscillation $S(\omega)$ is the Fourier transform of the two-time correlation function:

$$S(\omega) = \frac{1}{\pi}\,\mathrm{Re}\int_0^\infty d\tau \left\langle \hat{\sigma}_H^\dagger(t_{st}+\tau)\hat{\sigma}_H(t_{st})\right\rangle \exp(-i\omega\tau). \tag{3.4.22}$$

Calculation of such correlators is much easier if the system of Eqs. (3.4.19)–(3.4.21) can be rewritten as a linear system of first-order ordinary homogeneous differential equations with time-independent coefficients. Indeed, in this case, for an arbitrary operator column vector $\mathbf{x}(t)$ that obeys the equation

$$\frac{d\hat{\mathbf{x}}(t)}{dt} = \mathbf{M}\hat{\mathbf{x}}(t), \tag{3.4.23}$$

where $\mathbf{M}$ is a square constant c-number matrix, the two-time correlation function $\langle\hat{\mathbf{x}}(t+\tau)\hat{\mathbf{x}}(t)\rangle$ obeys the same equation as the vector $\hat{\mathbf{x}}(t)$:

$$\frac{d}{d\tau}\langle\hat{\mathbf{x}}(t+\tau)\hat{\mathbf{x}}(t)\rangle = \left\langle\frac{d}{d\tau}\hat{\mathbf{x}}(t+\tau)\hat{\mathbf{x}}(t)\right\rangle = \langle\mathbf{M}\hat{\mathbf{x}}(t+\tau)\hat{\mathbf{x}}(t)\rangle = \mathbf{M}\langle\hat{\mathbf{x}}(t+\tau)\hat{\mathbf{x}}(t)\rangle \tag{3.4.24}$$

If the equation for $\hat{\mathbf{x}}$ contains an external source $\hat{\mathbf{F}}(t)$ (as systems (3.4.19)–(3.4.21) do), in the equation for the two-time correlation function, the external force acquires the dependence on $\hat{\mathbf{x}}$ even if $\hat{\mathbf{F}}(t)$ is $\hat{\mathbf{x}}$-independent:

$$\begin{aligned}\frac{d}{d\tau}\langle\hat{\mathbf{x}}(t+\tau)\hat{\mathbf{x}}(t)\rangle &= \left\langle\frac{d}{d\tau}\hat{\mathbf{x}}(t+\tau)\hat{\mathbf{x}}(t)\right\rangle = \left\langle\mathbf{M}\hat{\mathbf{x}}(t+\tau)\hat{\mathbf{x}}(t) + \hat{\mathbf{F}}(t+\tau)\mathbf{x}(t)\right\rangle \\ &= \mathbf{M}\langle\hat{\mathbf{x}}(t+\tau)\hat{\mathbf{x}}(t)\rangle + \left\langle\hat{\mathbf{F}}(t+\tau)\hat{\mathbf{x}}(t)\right\rangle\end{aligned}$$

This complicates the search for $\langle\hat{\mathbf{x}}(t+\tau)\hat{\mathbf{x}}(t)\rangle$. However, if the sources are Markovian, then according to the quantum regression theorem (see Refs. [6, 21] and Problem 1.12.), we can still use Eq. (3.4.24). Therefore, our goal is to reduce the matrix of system (3.4.19)–(3.4.21) to a time-independent matrix in the desired form.

To make the coefficients in Eqs. (3.4.19)–(3.4.21) time-independent, the approach of slowly varying amplitudes can be applied:

$$\hat{\sigma}_{slow}(t) = \hat{\sigma}(t)\exp(i\omega_{ext}t), \qquad \hat{\sigma}^\dagger{}_{slow}(t) = \hat{\sigma}^\dagger(t)\exp(-i\omega_{ext}t). \tag{3.4.25}$$

Substituting Eq. (3.4.25) into Eqs. (3.4.19) – (3.4.21) we arrive at the following equations (the details of calculations can be found in Ref. [19]):

$$\frac{d\hat{\sigma}_{slow}}{dt} = (i(\omega_{ext}-\omega_\sigma)-\gamma_\sigma)\hat{\sigma}_{slow} - i\Omega_{ext}\hat{D} + \exp(i\omega_{ext}t)\hat{F}_\sigma(t), \tag{3.4.26}$$

$$\frac{d\hat{\sigma}^{\dagger}{}_{slow}}{dt} = (-i(\omega_{ext}-\omega_{\sigma})-\gamma_{\sigma})\hat{\sigma}^{\dagger}{}_{slow} + i\Omega_{ext}\hat{D} + \exp(-i\omega_{ext}t)\hat{F}_{\sigma^{\dagger}}(t), \quad (3.4.27)$$

$$\frac{d\hat{D}}{dt} = -\gamma_D\hat{D} + 2i\Omega_{ext}\left(\hat{\sigma}_{slow} - \hat{\sigma}^{\dagger}{}_{slow}\right) + \hat{F}_D - \gamma_D\hat{I}. \quad (3.4.28)$$

The next task is to exclude the non-Markovian source $-\gamma_D\,\hat{I}$ in Eq. (3.4.28). For this purpose, we resort to considering the expectation values of the operators. Since the system of Eqs. (3.4.26)–(3.4.28) is linear, these values obey the following system of equations:

$$\frac{d\langle\hat{\sigma}\rangle_{slow}}{dt} = (i(\omega_{ext}-\omega_{\sigma})-\gamma_{\sigma})\langle\hat{\sigma}\rangle_{slow} - i\Omega_{ext}\langle\hat{D}\rangle, \quad (3.4.29)$$

$$\frac{d\langle\hat{\sigma}^{\dagger}\rangle_{slow}}{dt} = (-i(\omega_{ext}-\omega_{\sigma})-\gamma_{\sigma})\langle\hat{\sigma}^{\dagger}\rangle_{slow} + i\Omega_{ext}\langle\hat{D}\rangle, \quad (3.4.30)$$

$$\frac{d\langle\hat{D}\rangle}{dt} = -\gamma_D(\langle\hat{D}\rangle + 1) + 2i\Omega_{ext}\left(\langle\hat{\sigma}\rangle_{slow} - \langle\hat{\sigma}^{\dagger}\rangle_{slow}\right). \quad (3.4.31)$$

When all transient processes are finished, and the system reaches its dynamic equilibrium, the stationary values of slowly varying amplitudes of system (3.4.26)–(3.4.28) become time-independent:

$$\begin{aligned}\langle\hat{\sigma}\rangle^{st}_{slow} &= \langle\hat{\sigma}^{\dagger}\rangle^{*st}_{slow} = \frac{-i\Omega_{ext}(\gamma_{\sigma}-i(\omega_{ext}-\omega_{\sigma}))}{\gamma_{\sigma}^2+(\omega_{ext}-\omega_{\sigma})^2+4\Omega_{ext}^2\gamma_{\sigma}/\gamma_D},\\ \langle\hat{D}\rangle^{st} &= -1+\frac{4\Omega_{ext}^2\gamma_{\sigma}/\gamma_D}{\gamma_{\sigma}^2+(\omega_{ext}-\omega_{\sigma})^2+4\Omega_{ext}^2\gamma_{\sigma}/\gamma_D}.\end{aligned} \quad (3.4.32)$$

Coming back to the full form of the solution, we obtain the following expressions:

$$\begin{aligned}\langle\hat{\sigma}\rangle^{st} &= \langle\hat{\sigma}^{\dagger}\rangle^{*st} = \frac{-i\Omega_{ext}(\gamma_{\sigma}-i(\omega_{ext}-\omega_{\sigma}))}{\gamma_{\sigma}^2+(\omega_{ext}-\omega_{\sigma})^2+4\Omega_{ext}^2\gamma_{\sigma}/\gamma_D}\exp(-i\omega_{ext}t)\\ \langle\hat{D}\rangle^{st} &= -\frac{\gamma_{\sigma}^2+(\omega_{ext}-\omega_{\sigma})^2}{\gamma_{\sigma}^2+(\omega_{ext}-\omega_{\sigma})^2+4\Omega_{ext}^2\gamma_{\sigma}/\gamma_D}.\end{aligned} \quad (3.4.33)$$

The first of these equations shows that the stationary behavior of the expectation value is a forced oscillation at the frequency of the external field.

Now, we are ready to exclude the source $-\gamma_D\hat{I}$ from Eq. (3.4.28). For this purpose, we transition to new variables:

$$\begin{aligned}\Delta\hat{\sigma}_{H\,slow}(t) &= \hat{\sigma}_{H\,slow}(t) - \langle\hat{\sigma}\rangle^{st}_{slow}\hat{I},\\ \Delta\hat{\sigma}^{\dagger}{}_{H\,slow}(t) &= \hat{\sigma}^{\dagger}{}_{H\,slow}(t) - \langle\hat{\sigma}^{\dagger}\rangle^{st}_{slow}\hat{I},\\ \Delta\hat{D}_H(t) &= \hat{D}_H(t) - \langle\hat{D}\rangle^{st}\hat{I}\end{aligned} \quad (3.4.34)$$

After substituting Eq. (3.4.34) into the system of Eqs. (3.4.26)–(3.4.28) and rewriting the system in the matrix form, we obtain:

$$\frac{d\hat{\mathbf{x}}(t)}{dt} = \mathbf{M}\hat{\mathbf{x}}(t) + \hat{\mathbf{F}},$$

where

$$\hat{\mathbf{x}} = \begin{pmatrix} \Delta\hat{\sigma}_{H\ slow}(t) \\ \Delta\hat{\sigma}^{\dagger}{}_{H\ slow}(t) \\ \Delta\hat{D}_H(t) \end{pmatrix}, \qquad \mathbf{M} = \begin{pmatrix} i(\omega_{ext} - \omega_\sigma) - \gamma_\sigma & 0 & -i\Omega_{ext} \\ 0 & -i(\omega_{ext} - \omega_\sigma) - \gamma_\sigma & i\Omega_{ext} \\ 2i\Omega_{ext} & -2i\Omega_{ext} & -\gamma_D \end{pmatrix},$$

$$\hat{\mathbf{F}} = \begin{pmatrix} e^{(i\omega_{ext}t)}\hat{F}_\sigma(t) \\ e^{(-i\omega_{ext}t)}\hat{F}_{\sigma^\dagger} \\ \hat{F}_D(t) \end{pmatrix},$$

the column source vector $\hat{\mathbf{F}}$ contains the Markovian source terms only.

To calculate the two-time correlators, such as $\left\langle \Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\hat{\sigma}_{slow}(t_{st}) \right\rangle$ (t_{st} is a characteristic time in which the system reaches the stationary state), we use the quantum regression theorem. This theorem states that if the sources are Markovian, the sought correlator can be found by solving a system of homogeneous equations having the matrix $\mathbf{A}$:

$$\frac{d}{d\tau}\begin{pmatrix} \left\langle \Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\hat{\sigma}_{slow}(t_{st}) \right\rangle \\ \left\langle \Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}) \right\rangle \\ \left\langle \Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\hat{D}(t_{st}) \right\rangle \end{pmatrix} = \mathbf{M}\begin{pmatrix} \left\langle \Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\hat{\sigma}_{slow}(t_{st}) \right\rangle \\ \left\langle \Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}) \right\rangle \\ \left\langle \Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\hat{D}(t_{st}) \right\rangle \end{pmatrix}. \tag{3.4.35}$$

The initial conditions for this system are (Problem 1.13)

$$\begin{aligned} \left\langle \Delta\hat{\sigma}^{\dagger}_{slow}(t_{st})\Delta\hat{\sigma}_{slow}(t_{st}) \right\rangle_{\tau=0} &= \left(1 + \left\langle \hat{D} \right\rangle^{st}\right)/2 - \left\langle \hat{\sigma}^{\dagger} \right\rangle^{st}_{slow}\left\langle \hat{\sigma} \right\rangle^{st}_{slow} \\ &= \frac{8\Omega^4_{ext}(\gamma_\sigma/\gamma_D)^2 + \Omega^2_{ext}\left(\gamma^2_\sigma + (\omega_{ext} - \omega_\sigma)^2\right)(2\gamma_\sigma/\gamma_D - 1)}{\left(\gamma^2_\sigma + (\omega_{ext} - \omega_\sigma)^2 + 4\Omega^2_{ext}\gamma_\sigma/\gamma_D\right)^2}, \end{aligned} \tag{3.4.36}$$

$$\left\langle \Delta\hat{\sigma}^{\dagger}_{slow}(t_{st})\Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}) \right\rangle = -\left(\left\langle \hat{\sigma}^{\dagger} \right\rangle^{st}_{slow}\right)^2 = \frac{\Omega^2_{ext}\left(\gamma^2_\sigma + (\omega_{ext} - \omega_\sigma)^2\right)}{\left(\gamma^2_\sigma + (\omega_{ext} - \omega_\sigma)^2 + 4\Omega^2_{ext}\gamma_\sigma/\gamma_D\right)^2}, \tag{3.4.37}$$

$$\left\langle \Delta\hat{\sigma}^{\dagger}_{slow}(t_{st})\Delta\hat{D}(t_{st})\right\rangle = -\left\langle\hat{\sigma}^{\dagger}\right\rangle^{st}_{slow}\left(1+\left\langle\hat{D}\right\rangle^{st}\right) = \frac{-4i\Omega^{3}_{ext}(\gamma_{\sigma}-i(\omega_{ext}-\omega_{\sigma}))\gamma_{\sigma}/\gamma_{D}}{\left(\gamma^{2}_{\sigma}+(\omega_{ext}-\omega_{\sigma})^{2}+4\Omega^{2}_{ext}\gamma_{\sigma}/\gamma_{D}\right)^{2}}. \tag{3.4.38}$$

According to Eq. (3.4.25), the operators $\hat{\sigma}_H(t)$ and $\hat{\sigma}^{\dagger}_H(t)$ can be expressed as

$$\hat{\sigma}_H(t) = \left(\left\langle\hat{\sigma}\right\rangle^{st}_{slow} + \Delta\hat{\sigma}_{slow}(t)\right)\exp(-i\omega_{ext}t)$$

and

$$\hat{\sigma}^{\dagger}_H(t) = \left(\left\langle\hat{\sigma}^{\dagger}\right\rangle^{st}_{slow} + \Delta\hat{\sigma}^{\dagger}{}_{slow}(t)\right)\exp(i\omega_{ext}t).$$

This gives the following equation for the two-time correlator:

$$\left\langle\hat{\sigma}^{\dagger}(t_{st}+\tau)\hat{\sigma}(t_{st})\right\rangle = \left|\left\langle\hat{\sigma}\right\rangle^{st}_{slow}\right|^{2}\exp(i\omega_{ext}\tau) + \left\langle\Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\hat{\sigma}_{slow}(t_{st})\right\rangle\exp(i\omega_{ext}\tau). \tag{3.4.39}$$

The first term in this expression gives the δ-shape contribution to the spectrum. Usually, this term is considered to be responsible for the coherent elastic Rayleigh scattering at the frequency of the external field ω_{ext}. For this reason, it is often called the coherent or elastic part of the oscillations.

The second term in Eq. (3.4.39) is the contribution due to quantum fluctuations in the TLS. This is not only noises but also terms appearing due to the noncommutative properties of the operators (see Eq. (2.4.13)). From matrix eq. (3.4.35), it follows that

$$\frac{d}{d\tau}\left\langle\Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\hat{\sigma}_{slow}(t_{st})\right\rangle = [(\omega_{ext}-\omega_{\sigma})-\gamma_{\sigma}]\left\langle\Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\hat{\sigma}_{slow}(t_{st})\right\rangle - i\Omega_{ext}\left\langle\Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\hat{D}(t_{st})\right\rangle$$

This equation shows that $\left\langle\Delta\hat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\hat{\sigma}_{slow}(t_{st})\right\rangle$ depends on τ as $\exp(-\gamma_{\sigma}\tau)$. Thus, the last term in Eq. (3.4.39) determines the spectrum width. This term can be called the incoherent or inelastic part of the TLS oscillations.

The spectrum of the TLS oscillations is determined by the Wiener-Khinchin theorem (Eq. (3.4.22)). Using Eqs. (3.4.25) and (3.4.39), we can divide the spectrum into coherent and incoherent parts:

$$S(\omega) = S_{coh}(\omega) + S_{incoh}(\omega). \tag{3.4.40}$$

where the coherent part is produced by the driven oscillations of the TLS polarization σ

$$S_{coh}(\omega) = \frac{1}{\pi} \mathrm{Re} \int_0^\infty d\tau \left| \langle \hat{\sigma} \rangle_{slow}^{st} \right|^2 \exp(-i(\omega - \omega_{ext})\tau), \tag{3.4.41}$$

while the incoherent part is determined by quantum fluctuations of the TLS polarization operator:

$$S_{incoh}(\omega) = \frac{1}{\pi} \mathrm{Re} \int_0^\infty d\tau \left\langle \Delta\hat{\sigma}_{slow}^{\dagger}(t_{st} + \tau)\Delta\hat{\sigma}_{slow}(t_{st}) \right\rangle \exp(-i(\omega - \omega_{ext})\tau). \tag{3.4.42}$$

The contribution of the incoherent term becomes significant if the amplitude of the incident field is large enough so that, $\Omega_{ext} > \gamma_D$ (see Refs. [6, 7] and the discussion below).

The term $\left\langle \Delta\hat{\sigma}_{slow}^{\dagger}(t_{st} + \tau)\Delta\hat{\sigma}_{slow}(t_{st}) \right\rangle$ is often considered as an inelastic contribution [7] because the corresponding Fourier transform differs from the delta-function. However, in the literature on Raman scattering, the contributions at the Stokes and anti-Stokes frequencies are called inelastic, while the contributions to the spectrum near the frequency of the incident field (even with a finite linewidth) are called elastic. In this book, we follow the terminology customary for the literature on Raman scattering and call inelastic only those contributions to the spectrum arising from the coupling with vibrations of nuclei in a molecule. The term $\left\langle \Delta\hat{\sigma}_{slow}^{\dagger}(t_{st} + \tau)\Delta\hat{\sigma}_{slow}(t_{st}) \right\rangle$ is referred to as incoherent.

To conclude this subsection, we have found the dynamics of the TLS, which is driven by the external monochromatic field and radiates into free space. In the next subsection, we show that the spectrum of the emitted field up to a constant coincides with the spectrum of TLS dynamics.

3.4.2 *The Radiation Spectrum of Driven Two-Level System in the Heisenberg Picture*

There are two experimental methods for determining the spectrum of radiation. One is passing light through an optical prism or diffraction grating to obtain the Fourier harmonics of the signal. Then, one can separately measure the light intensity of each Fourier harmonic. In such experiments, the measured quantity is proportional to the average number of photons $n_{\mathbf{k}}(t) = \left\langle \hat{a}_{\mathbf{k}}^{\dagger}(t)\hat{a}_{\mathbf{k}}(t) \right\rangle$ in the mode with the given wave vector $\mathbf{k}$ and the polarization α (to simplify the notations, below, we drop the subscript α).

To find $n_{\alpha,\,\mathbf{k}}(t)$, we assume that, first, the TLS exhibits forced oscillations of the dipole moment caused by the external field and, second, at any time, the average number of emitted photons is much less than unity. This means that the excitation of the free space mode does not affect the TLS radiation rate. In other words, we neglect the back action of the radiated photons on the TLS.

Using Hamiltonian (3.4.14), we can write the Heisenberg equation for the annihilation operator $\hat{a}_{\mathbf{k}}$:

$$\frac{d\hat{a}_{\mathbf{k}}(t)}{dt} = \frac{i}{\hbar}\left[\hat{H}, \hat{a}_{\mathbf{k}}\right] = -i\omega_{a,\mathbf{k}}\hat{a}_{\mathbf{k}}(t) - i\sqrt{\frac{2\pi\omega_{a,\mathbf{k}}}{V\hbar}}\mathbf{e}_{\alpha\mathbf{k}} \cdot \mathbf{d}_{eg}\hat{\sigma}_H(t), \tag{3.4.43}$$

where $\mathbf{e}_{\alpha\mathbf{k}}$ is the unit vector of the electric field with the polarization α. The integration of Eq. (3.4.43) gives:

$$\hat{a}_{\mathbf{k}}(t) = \hat{a}_{\mathbf{k}}(0)\exp(-i\omega_{a,\mathbf{k}}t) - i\sqrt{\frac{2\pi\omega_{a,\mathbf{k}}}{V\hbar}}\mathbf{e}_{\mathbf{k}} \cdot \mathbf{d}_{eg}\int_0^t d\tau\hat{\sigma}_H(\tau)\exp(-i\omega_{a,\mathbf{k}}(t-\tau)) \tag{3.4.44}$$

The first term on the right-hand side of Eq. (3.4.44) describes the evolution of free space mode, and the second term describes the field scattered by the TLS. The expectation value of the photon number in each mode is

$$\begin{aligned} n_{\mathbf{k}}(t) \equiv \left\langle \hat{a}_{\mathbf{k}}^{\dagger}(t)\hat{a}_{\mathbf{k}}(t)\right\rangle &= \left\langle \hat{a}_{\mathbf{k}}^{\dagger}(0)\hat{a}_{\mathbf{k}}(0)\right\rangle \\ &+ \sqrt{\frac{2\pi\omega_{a,\mathbf{k}}}{V\hbar}}\mathbf{e}_{\mathbf{k}} \cdot \mathbf{d}_{eg}\left(-i\int_0^t d\tau\left\langle \hat{a}_{\mathbf{k}}^{\dagger}(0)\hat{\sigma}_H(\tau)\right\rangle \exp(-i\omega_{a,\mathbf{k}}(t-\tau))\right. \\ &\left. + i\int_0^t d\tau\left\langle \hat{\sigma}_H^{\dagger}(\tau)\hat{a}_{\mathbf{k}}(0)\right\rangle \exp(i\omega_{a,\mathbf{k}}(t-\tau))\right) \\ &+ \left|\sqrt{\frac{2\pi\omega_{a,\mathbf{k}}}{V\hbar}}\mathbf{e}_{\mathbf{k}} \cdot \mathbf{d}_{eg}\right|^2 \int_0^t d\tau_2\int_0^t d\tau_1\left\langle \hat{\sigma}_H^{\dagger}(\tau_2)\hat{\sigma}_H(\tau_1)\right\rangle \exp(-i\omega_{a,\mathbf{k}}(\tau_2-\tau_1)) \end{aligned} \tag{3.4.45}$$

Suppose the TLS reaches the stationary regime, in which oscillations are driven (Eqs. (3.4.36)–(3.4.38)). We also assume that at the initial moment, the reservoir of the free space mode is in thermal equilibrium, i.e., $\left\langle \hat{a}_{\mathbf{k}}^{\dagger}(0)\hat{a}_{\mathbf{k}}(0)\right\rangle = \overline{n}_T$. Then, Eq. (3.4.45) is simplified to

$$
\begin{aligned}
n_{\mathbf{k}}(t) &= \overline{n}_T + \left|\sqrt{\frac{2\pi\omega_{\mathbf{k}}}{V\hbar}}\mathbf{e}_{\mathbf{k}}\cdot\mathbf{d}_{eg}\right|^2 \int_0^t d\tau_2 \int_0^t d\tau_1 \left\langle \hat{\sigma}_H^{\dagger}(\tau_2)\hat{\sigma}_H(\tau_1)\right\rangle \exp(-i\omega_{\mathbf{k}}(\tau_2-\tau_1)) \\
&= \overline{n}_T + \left|\sqrt{\frac{2\pi\omega_{\mathbf{k}}}{V\hbar}}\mathbf{e}_{\mathbf{k}}\cdot\mathbf{d}_{eg}\right|^2 \left(\left|\left\langle \hat{\sigma}_{slow}^{st}\right\rangle\right|^2 \int_0^t d\tau_2 \int_0^t d\tau_1 \exp(i(\omega_{ext}-\omega_{\mathbf{k}})(\tau_2-\tau_1)) \right. \\
&\quad \left. + \int_0^t d\tau_2 \int_0^t d\tau_1 \left\langle \Delta\hat{\sigma}^{\dagger}\Delta\hat{\sigma}(\tau_2-\tau_1)\right\rangle \exp(i(\omega_{ext}-\omega_{\mathbf{k}})(\tau_2-\tau_1)) \right) \\
&= \overline{n}_T + \left|\sqrt{\frac{2\pi\omega_{\mathbf{k}}}{V\hbar}}\mathbf{e}_{\mathbf{k}}\cdot\mathbf{d}_{eg}\right|^2 \left(t\left|\left\langle \hat{\sigma}_{slow}^{st}\right\rangle\right|^2 2\pi\delta(\omega_{ext}-\omega_{\mathbf{k}}) + t\pi S_{incoh}(\omega_{\mathbf{k}})\right)
\end{aligned}
\tag{3.4.46}
$$

where $S_{incoh}(\omega)$ is the spectrum of the incoherent TLS oscillations, determined by Eq. (3.4.42).

The first term in Eq. (3.4.46) is the number of thermal photons of free space. The second term is proportional to the stationary value of the induced dipole moment of the TLS, $|\langle\hat{\sigma}_{st}\rangle|^2$. This term arises due to the coherent forced oscillation, and it corresponds to the Rayleigh scattering. The third term corresponds to the incoherent fluorescence accompanying the coherent Rayleigh scattering (the Mollow triplet), which is discussed in the next section in detail.

The second method of measuring the light spectrum uses an interferometer. In this method, incident light with the amplitude $\mathbf{E}(t)$ passes through a beam splitter. The obtained two beams with amplitudes $\hat{\mathbf{E}}_1(t)$ and $\hat{\mathbf{E}}_2(t)$ run along two different optical paths, say r_1 and r_2. As a result, one of the beams gains the retardation time $\tau = (r_1 - r_2)/c$, so that $\hat{\mathbf{E}}_1(t) = \hat{\mathbf{E}}_2(t+\tau)$. The beams converge on the detector, which measures the intensity of the incident light. Knowing the total intensity and the intensities of both beams, one can obtain the correlator:

$$
\left\langle \hat{\mathbf{E}}^{\dagger}(\mathbf{r}_1,t)\cdot\hat{\mathbf{E}}(\mathbf{r}_2,t)\right\rangle \sim \left\langle \hat{\mathbf{E}}^{\dagger}(t)\cdot\hat{\mathbf{E}}(t+\tau)\right\rangle \tag{3.4.47}
$$

The Fourier transform of this correlator is proportional to $S(\omega)$ given by Eq. (3.4.42). To prove this, we note that the total emitted field of each mode is the sum of plane waves with the wave vectors $\mathbf{k}$ and the polarizations α:

$$
\hat{\mathbf{E}}(\mathbf{r},t) = \sum_{\mathbf{k}} \hat{\mathbf{E}}_{\mathbf{k}}(\mathbf{r},t) = \sum_{\mathbf{k}} \sqrt{\frac{2\pi\hbar\omega_{a,\mathbf{k}}}{V}}\mathbf{e}_{\mathbf{k}}\hat{a}_{\mathbf{k}}(t)e^{i\mathbf{k}\mathbf{r}} \tag{3.4.48}
$$

In this equation, replacing $\hat{a}_{\mathbf{k}}$ with the expression given by Eq. (3.4.44), for the total radiated field, we obtain:

$$\hat{\mathbf{E}}(\mathbf{r},t) = -i\sum_{\mathbf{k}} \frac{2\pi\omega_{a,\mathbf{k}}}{V} e^{i\mathbf{kr}} \mathbf{e}_{\mathbf{k}} \left(\mathbf{e}_{\mathbf{k}} \cdot \mathbf{d}_{eg}\right) \int_0^t d\tau \hat{\sigma}_H(\tau) e^{-i\omega_{a,\mathbf{k}}(t-\tau)} \tag{3.4.49}$$

Now, replacing the summation with the integration

$$\sum_{\mathbf{k}} \to \frac{V}{(2\pi)^3} \int d^3\mathbf{k} = \frac{V}{(2\pi)^3} \int_0^{\infty} dk k^2 \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi,$$

and separating the slowly varying amplitude of the operator $\hat{\sigma}_H$: $\hat{\sigma}_H(t) = \hat{\sigma}_{H\,slow} \exp(-i\omega_{\text{ext}} t)$, we can transform Eq. (3.4.49) into

$$\begin{aligned} \hat{\mathbf{E}}(\mathbf{r},t) \; = \; & \frac{-ie(-i\omega_{\text{ext}}t)}{(2\pi)^2 c^3} \int_0^{\infty} d\omega \omega^3 \int_0^{\pi} d\theta \sin\theta \\ & \times \int_0^{2\pi} d\varphi \sum_{\alpha} \mathbf{e}_{\mathbf{k}} \left(\mathbf{e}_{\mathbf{k}} \mathbf{d}_{eg}\right) \exp\left(i\omega \frac{r}{c} \cos\theta\right) \int_0^t d\tau \hat{\sigma}_{H\,slow}(\tau) \exp\left(-i(\omega - \omega_{\text{ext}})(t-\tau)\right) \end{aligned} \tag{3.4.50}$$

The summation over the polarizations of the plane waves gives $\sum_{\mu} \mathbf{e}_{\mathbf{k},\mu} \left(\mathbf{e}_{\mathbf{k},\mu} \cdot \mathbf{d}_{eg}\right)$ $= \left[\mathbf{k}, \left[\mathbf{k}, \mathbf{d}_{eg}\right]\right]/k^2$ [40]. Further, we can perform the integration over angles and arrive at the following expression:

$$\begin{aligned} \hat{\mathbf{E}}(\mathbf{r},t) \; = \; & \frac{\left[\mathbf{n}, \left[\mathbf{n}, \mathbf{d}_{eg}\right]\right]}{2\pi c^2 r} \\ & \times \left(\exp\left(-i\omega_{\text{ext}}\left(t - \frac{r}{c}\right)\right) \int_0^t d\tau \hat{\sigma}_{H\,slow}(\tau) \int_0^{\infty} d\omega \omega^2 e\left(-i(\omega - \omega_{\text{ext}})\left(t - \frac{r}{c} - \tau\right)\right) \right. \\ & \left. - \exp\left(-i\omega_{\text{ext}}\left(t + \frac{r}{c}\right)\right) \int_0^t d\tau \hat{\sigma}_{H\,slow}(\tau) \int_0^{\infty} d\omega \omega^2 \exp\left(-i(\omega - \omega_{\text{ext}})\left(t + \frac{r}{c} - \tau\right)\right) \right) \end{aligned} \tag{3.4.51}$$

where $\mathbf{n} = \mathbf{k}/k$. Fourier-type integral (3.4.51) can be evaluated by using the method of the stationary phase [41] in the vicinity of $\omega = \omega_{\text{ext}}$ which results in the following expression for $\hat{\mathbf{E}}(\mathbf{r},t)$:

$$\hat{\mathbf{E}}(\mathbf{r},t) \approx \frac{\left[\mathbf{n},\left[\mathbf{n},\mathbf{d}_{eg}\right]\right]}{2\pi c^2 r}$$
$$\times\left(\exp\left(-i\omega_{\text{ext}}\left(t-\frac{r}{c}\right)\right)\omega_{ext}^2\int_0^t d\tau\hat{\sigma}_{H\,slow}(\tau)\int_{-\infty}^{\infty}d\omega\exp\left(-i(\omega-\omega_{ext})\left(t-\frac{r}{c}-\tau\right)\right)\right.$$
$$\left.-\exp\left(-i\omega_{\text{ext}}\left(t+\frac{r}{c}\right)\right)\omega_{ext}^2\int_0^t d\tau\hat{\sigma}_{H\,slow}(\tau)\int_{-\infty}^{\infty}d\omega\exp\left(-i(\omega-\omega_{\text{ext}})\left(t+\frac{r}{c}-\tau\right)\right)\right)$$
$$=\frac{\left[\mathbf{n},\left[\mathbf{n},\mathbf{d}_{eg}\right]\right]}{2\pi c^2 r}\left(\exp\left(-i\omega_{\text{ext}}\left(t-\frac{r}{c}\right)\right)\omega_{ext}^2\int_0^t d\tau\hat{\sigma}_{H\,slow}(\tau)2\pi\delta\left(t-\frac{r}{c}-\tau\right)\right.$$
$$\left.-\exp\left(-i\omega_{ext}\left(t+\frac{r}{c}\right)\right)\omega_{\text{ext}}^2\int_0^t d\tau\hat{\sigma}_{H\,slow}(\tau)2\pi\delta\left(t+\frac{r}{c}-\tau\right)\right)$$
$$=\exp\left(-i\omega_{ext}\left(t-\frac{r}{c}\right)\right)\frac{\omega_{\text{ext}}^2\left[\mathbf{n},\left[\mathbf{n},\mathbf{d}_{eg}\right]\right]}{c^2 r}\hat{\sigma}_{H\,slow}\left(t-\frac{r}{c}\right)$$
$$=\frac{\omega_{ext}^2\left[\mathbf{n},\left[\mathbf{n},\mathbf{d}_{eg}\right]\right]}{c^2 r}\hat{\sigma}_H\left(t-\frac{r}{c}\right) \tag{3.4.52}$$

We see that the operator of the electric field is proportional to the operator of the atomic dipole moment, $\hat{E}(t)\sim\hat{\sigma}(t-r/c)$. In the far-field zone, the radiated field determined by Eq. (3.4.52) coincides with the one radiated by a classical dipole, $\mathbf{E}=\omega^2[\mathbf{n}[\mathbf{n},\mathbf{d}(t-r/c)]]/cr^2$.

According to Eqs. (3.4.47) and (3.4.52)

$$\left\langle\hat{\mathbf{E}}^{\dagger}(\mathbf{r}_1,t)\cdot\hat{\mathbf{E}}(\mathbf{r}_2,t)\right\rangle=\left|\sqrt{\frac{2\pi\omega_{\mathbf{k}}}{V\hbar}}\mathbf{e}_{\mathbf{k}}\cdot\mathbf{d}_{eg}\right|^2\left\langle\hat{\sigma}^{\dagger}(t)\hat{\sigma}(t+\tau)\right\rangle. \tag{3.4.53}$$

In other words, the spectrum of scattered radiation $S_{sr}(\omega)$ is the Fourier transformation of the correlator $\left\langle\hat{\mathbf{E}}^{\dagger}(\mathbf{r}_1,t)\cdot\hat{\mathbf{E}}(\mathbf{r}_2,t)\right\rangle$ [42, 43]. Equation (3.4.53) shows that these correlators are linearly connected. Consequently, $S_{sr}(\omega)$ is proportional to the spectrum S of TLS dipole oscillations (see Eq. (3.4.46)):

$$S_{sr}=n_{\mathbf{k}}(t)/t=\overline{n}_T+\left|\sqrt{\frac{2\pi\omega_{\mathbf{k}}}{V\hbar}}\mathbf{e}_{\mathbf{k}}\cdot\mathbf{d}_{eg}\right|^2\left(\left|\left\langle\hat{\sigma}_{slow}^{st}\right\rangle\right|^2 2\pi\delta(\omega_{ext}-\omega_{\mathbf{k}})+\pi S(\omega_{\mathbf{k}})\right) \tag{3.4.54}$$

The Fourier transform of this equation is the same as Eq. (3.4.42).

The radiation spectrum appears as a perturbation of the free space modes. The perturbation is determined by Eq. (3.4.43) and, up to a constant factor, coincides with the spectrum $S(\omega)$ of the dipole moment oscillation of the TLS (see Eq. (3.4.42)). Thus, to calculate the radiation spectrum, it is sufficient to calculate the oscillation spectrum of the atomic dipole moment.

To conclude Chap. 3, we summarize the obtained results. We have seen that the irreversibility of the transition of an atom from an excited state to a ground state occurs when the atom interacts with a continuum of reservoir modes with a given energy and all possible directions of wave vectors. For photon radiation, this reservoir is the reservoir of free space modes, while for photon absorption, this reservoir is the ensemble of final atomic states. In the former case, the lost energy is distributed among the reservoir modes. If we deal with a finite number of reservoir modes, the modes should be included in the unified Hermitian system, which loses no energy and does not reach a stationary state.

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Chapter 4
Coherent Light

Before proceeding to the quantum theory of Rayleigh scattering, we must clarify what we mean by coherence. In the literature, there are two approaches to describing coherence. The first approach treats the light as a classical EM field [1], while the second deals with quantized fields [2]. Generally speaking, interpretations of the concept of "coherence" given by these approaches are not identical.

In classical physics, the coherence of two signals is understood as their ability to generate an interference pattern. To assess the coherence of a light beam, it can be split into two beams, and their potential for interference is examined. To achieve this, the beams must go through different optical paths from the point of separation to the point where their combined intensity is recorded. The contrast of the interference pattern quantifies the degree of coherence. In this sense, a monochromatic plane wave is perfectly coherent.

Defining coherence for quantum fields is more complicated; we discuss it below. In many experiments, EM fields behave as a composition of quanta of the EM field (photons). To describe photons, amplitudes of classical EM fields are replaced with operators. While classical EM fields are characterized by directly measurable c-functions, the quantized fields are characterized by the wave function or quantum states. In experiment, one can measure the expectation values of the operators corresponding to EM fields.

It is usually assumed that the transition from the quantum description to the classical one occurs when the number of photons is large. Unlike classical quantities, the operators corresponding to the EM fields may not commute. However, since commutators of the field operators are proportional to the Planck constant, we can treat these operators as c-numbers. The expectation values of the field operators become almost continuous variables of the number of photons. The quantization becomes immaterial, and we can set $\hbar = 0$.

The quantum nature of light is most clearly manifested when describing the quantum states of light using Fock states—the states having a fixed number of light quanta (photons). However, in doing so, we encounter some problems with the transition to the classical description.

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First, a Fock state with a single-photon incident on two holes in a screen does not produce an interference picture on the plane of a receiver behind the screen. Only by repeating this experiment many times can we see the interference pattern. The situation changes dramatically if we consider a Fock state with two incident quanta. There is a possibility that we will not observe the interference picture at all (Hong-Ou-Mandel effect) [3]. Thus, the more quanta a Fock state has, the more difficult it is to interpret its coherence according to the classical definition. That contradicts our expectations of the transition to the classical description with an increase in the number of photons.

Second, even for a Fock state with many photons, the expectation values of the creation and annihilation operators and, consequently, the expectation values of the field operator $\widehat{E}(z) = E_0(z)\left(\widehat{a}^\dagger + \widehat{a}\right)$ are zero.

We can expect that the contradiction between classical and quantum approaches to coherence is due to using the basis of Fock states, for which the expectation values of the field are zero—using a different basis should fix the problem. This basis should be such that the expectation values of the electric field are not equal to zero. Below, we show that the eigenstates $|z\rangle$ of the annihilation operator $\widehat{a}$ ($\widehat{a}|z\rangle = z|z\rangle$) meet this requirement, and in quantum optics, they are considered as coherent states [4]. We discuss the properties of the states which justify such a name. In particular, we show that though the annihilation operator is not Hermitian, its eigenfunctions can build a basis. However, since the operator $\widehat{a}$ is not Hermitian, this basis is not orthonormal and is overcomplete.

To describe the properties of such eigenstates, it is convenient to use a unitary operator of a shift in the phase space (Problem 1.14):

$$\begin{aligned}\widehat{D}(z) &= \exp\left(z\widehat{a}^\dagger - z^*\widehat{a}\right) = \exp\left[\left(\widehat{a}^\dagger - \widehat{a}\right)\mathrm{Re}\, z + i\left(\widehat{a}^\dagger + \widehat{a}\right)\mathrm{Im} z\right] \\ &= \exp\left[i\left(p_0\widehat{Q} - q_0\widehat{P}\right)/\hbar\right] = \widehat{D}(q_0, p_0).\end{aligned} \tag{4.1.1}$$

Here the operators $\widehat{Q}$ and $\widehat{P}$ are quadrature operators used for the quantization of the EM field in Sect. 2.5, $q_0 = \sqrt{2\hbar/\omega}\,\mathrm{Re}\, z$ and $p_0 = \sqrt{2\hbar\omega}\mathrm{Im} z$. One can see that $D^\dagger(z) = D^{-1}(z)D(-z)$. The expectation values of the quadrature operators $\widehat{Q}$ and $\widehat{P}$ in a coherent state are $\langle z|\widehat{Q}|z\rangle = \langle 0|\widehat{D}^\dagger(z)\widehat{Q}\widehat{D}(z)|0\rangle = \langle 0|\widehat{Q} - q_0\widehat{1}|0\rangle = q_0$ and $\langle z|\widehat{P}|z\rangle = p_0$, respectively (see Problem 1.15).

Thanks to the operator $\widehat{D}(z)$, further analytical calculations become easier. Particularly, the coherent state can also be determined as a result of the action of the operator on the vacuum state:

$$|z\rangle = \widehat{D}(z)|0\rangle. \tag{4.1.2}$$

Indeed, the coherent state defined in this way is an eigenfunction of the annihilation operator. This can be seen from the equality chain:

$$0 = \widehat{D}(z)\widehat{a}|0\rangle = \widehat{D}(z)\widehat{a}\widehat{D}^{-1}(z)|z\rangle = \left(\widehat{a} - z\widehat{1}\right)|z\rangle, \tag{4.1.3}$$

in which $\widehat{a}|0\rangle = 0|0\rangle$ is taken into account (see Problem 1.16). Equation (4.1.3) indicates that the coherent state is the eigenfunction of the annihilation operator, $\widehat{a}|z\rangle = z|z\rangle$.

As shown in Problem 1.17, the coherent state can be expanded over the Fock states [2]:

$$|z\rangle = \widehat{D}(z)|0\rangle = \exp\left(\frac{1}{2}|z|^2\right)\sum \frac{z^n}{\sqrt{n!}}|n\rangle \tag{4.1.4}$$

Even though the coherent states are not orthogonal

$$|\langle z|z'\rangle| = \exp\left(-\frac{1}{2}|z - z'|^2\right), \tag{4.1.5}$$

they can comprise a basis in the Hilbert space of the quantum states $|\psi\rangle$ of the EM field:

$$\frac{1}{\pi}\int d^2 z|z\rangle\langle z'| = \widehat{1} \tag{4.1.6}$$

$$|\psi\rangle = \widehat{I}|\psi\rangle = \frac{1}{\pi}\int d^2 z|z\rangle\langle z|\psi\rangle \tag{4.1.7}$$

(see Problem 1.18).

It is worth emphasizing that at $|\langle z|z^{'}\rangle| \to \infty$, the states become orthogonal, while at $|\langle z|z^{'}\rangle| \to 0$, they are almost the same. This feature is inherent to classical fields. A small difference in photon numbers weakly influences the field structure.

After the Hermitian conjugation, we obtain $\langle z|\widehat{a}^{\dagger} = z^*\langle z|$. Then, if we search for the expectation value over the coherent state of the normally ordered product of any real and analytic functions of the creation and annihilation operators (i.e., in the product, all the creation operators are on the left of the annihilation operators), the expectation value is reduced to the product of the function:

$$\langle z|f\left(\widehat{a}^{\dagger}\right)g(\widehat{a})|z\rangle = \langle f(a)z|g(\widehat{a})|z\rangle = f(z^*)g(z) \tag{4.1.8}$$

This property relates the quantum concepts of coherence to the classical one. To see this, we consider the process of photon detection.

In most experiments, photon detection is reduced to registering the current of electrons arising due to the ionization of an atom absorbing a photon. It is assumed that the system of the atom-EM field is initially in the state ψ_i which has a photon that can ionize the atom and the atom in the ground state.

Usually, the electric field operator in the Heisenberg picture

$$\widehat{\mathbf{E}}(\mathbf{x},t)=\sum\nolimits_m(2\pi\hbar\omega_m)^{1/2}\left[a_m^{\dagger}e^{i\omega_m t}+a_m e^{-i\omega_m t}\right]\mathbf{u}_m(\mathbf{x}) \tag{4.1.9}$$

can be represented as the sum of two terms, called components with positive:

$$\left(\widehat{\mathbf{E}}^{(-)}\right)=\sum\nolimits_m(2\pi\hbar\omega_m)^{1/2}\left[\widehat{a}_m^{\dagger}e^{i\omega_m t}\right]\mathbf{u}_m(\mathbf{x}) \tag{4.1.10}$$

and negative

$$\left(\widehat{\mathbf{E}}^{(+)}\right)=\sum\nolimits_m(2\pi\hbar\omega_m)^{1/2}\left[\widehat{a}_m e^{-i\omega_m t}\right]\mathbf{u}_m(\mathbf{x}) \tag{4.1.11}$$

Fourier frequencies.

To ionize the atom, only the contribution of the components of the field operator with negative frequencies $\widehat{\mathbf{E}}^{(+)}$, which contains operators of annihilation (absorption) of photons, is significant. Consequently, the zero-field oscillations do not contribute to this process because the action of the annihilation operator on them gives zero.

For ionization, the conditions for the applicability of Fermi's golden rule are satisfied (see Eq. (3.3.6)), and the probability of ionization is equal to [5]:

$$\int_0^t\exp(i\omega_{fi}\tau)\sum_f\left|\langle\psi_f|\widehat{\mathbf{E}}^{(+)}|\psi_i\rangle\right|^2d\tau=\int_0^t\int_0^t\exp(i\omega_{fi}(t'-t''))\sum_f\langle\psi_i|\widehat{\mathbf{E}}^{(+)}(t')|\psi_f\rangle^{\dagger}\langle\psi_i|\widehat{\mathbf{E}}^{(+)}(t'')|\psi_f\rangle dt'dt''$$

$$\underset{\left(\widehat{\mathbf{E}}^{(+)}\right)^*=\widehat{\mathbf{E}}^{(-)}}{=}\int_0^t\int_0^t\exp(i\omega_{fi}(t'-t''))\sum_f\langle\psi_i|\widehat{\mathbf{E}}^{(-)}(t')|\psi_f\rangle\langle\psi_f|\widehat{\mathbf{E}}^{(+)}(t'')|\psi_i\rangle\exp(i\omega_{fi}(t'-t''))dt'dt''.$$

Since $\sum_f|\psi_f\rangle\langle\psi_f|=1$, the integrand is proportional to $\left\langle\widehat{\mathbf{E}}^{(+)}(t')\cdot\widehat{\mathbf{E}}^{(+)}(t'')\right\rangle$. For the coherent state, the correlation function takes the trivial form (see Eq. (4.1.8)):

$$\left\langle\widehat{\mathbf{E}}^{(-)}(t')\cdot\widehat{\mathbf{E}}^{(+)}(t'')\right\rangle=\left\langle\widehat{\mathbf{E}}^{(-)}(t')\right\rangle\cdot\left\langle\widehat{\mathbf{E}}^{(+)}(t'')\right\rangle.$$

This corresponds to the expression in the classical definition of the intensity $\widehat{\mathbf{E}}^*\cdot\widehat{\mathbf{E}}$ of a monochromatic wave. Consequently, the quantum coherent state and the classical monochromatic wave have the same correlation functions equal to unity.

There is a more evident connection between quantum coherent states and classical monochromatic waves. Since the electric field operator in the Heisenberg picture has the form

$$\widehat{\mathbf{E}}(\mathbf{x},t)=\sum\nolimits_m(2\pi\hbar\omega_m)^{1/2}\left[\widehat{a}^{\dagger}e^{i\omega_m t}+\widehat{a}e^{-i\omega_m t}\right]\mathbf{u}_m(\mathbf{x}),$$

the expectation value of the electric field in the coherent state is

$$\langle z|\widehat{\mathbf{E}}(\mathbf{x},t)|z\rangle = (2\pi\hbar\omega)^{1/2}\left[z^* e^{i\omega_m t} + z e^{-i\omega_m t}\right]\mathbf{u}(\mathbf{x}).$$

This expression is exactly the same as the expression for a classical plane wave. Thus, in terms of expectation values, the classical and quantum definitions of coherence coincide. Since, in the absence of noise, the correlation function of classical electric fields also gives us the product of the fields, below, we call noiseless classical fields coherent.

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Chapter 5
Semi-Classical Description of Rayleigh Light Scattering

In classical electrodynamics, the dipole moment of a subwavelength particle behaves like a linear oscillator. In particular, the forced oscillations of the induced dipole moment always occur at the frequency of an external force. Consequently, when such particles scatter a monochromatic EM wave, the frequency of the scattered light remains the same as the frequency of the incident light. Thus, classical theory predicts that the spectrum of the Rayleigh scattering is a delta-function.

In Chap. 2, we have seen that if a TLS interacts with a single mode of a classical monochromatic field, it performs the Rabi oscillations without emitting or absorbing photons. In particular, employing Eqs. (2.4.13)–(2.4.15) for $\widehat{\sigma}_H^{\dagger}(t)$ and $\widehat{\sigma}_H(t)$, we can find an estimation for the correlation function:

$$\left\langle \widehat{\sigma}_H^{\dagger}(t+\tau)\widehat{\sigma}_H(t)\right\rangle = \frac{1}{4}\exp(i\omega_{ext}\tau)[1+\cos(2\Omega_{ext}\tau)]. \tag{5.1.1}$$

As was mentioned in Sect. 3.4, the radiation spectrum of the TLS oscillations is determined by the Wiener-Khinchin theorem. In particular, the spectrum is proportional to the Fourier transformation of this correlation function. For the correlation function determined by Eq. (5.1.1), the spectrum contains three delta-functions at the frequencies ω_{ext} and $\omega_{ext} \pm 2\Omega_{ext}$. This contradicts Rayleigh's theory.

More rigorous calculations are required to consider a TLS as an open system interacting with a reservoir of the free space modes. The dynamics of $\widehat{\sigma}_H^{\dagger}(t)$ and $\widehat{\sigma}_H(t)$ is described by the Heisenberg-Langevin equations. The correlation function $\left\langle \widehat{\sigma}_H^{\dagger}(t+\tau)\widehat{\sigma}_H(t)\right\rangle$ can be found by employing the quantum regression theorem (see Sect. 3.4).

Following this way, in the next subsections, we show that for strong coupling ($\Omega_{ext} \gg \gamma_D$), one can distinguish three characteristic frequencies (the Mollow triplet), while for weak coupling, only one delta-function arises.

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Special attention will also be paid to the TLS interaction with reservoirs, the properties of which can significantly differ from the properties of the reservoir of free space modes. For example, light scattering by colloidal quantum dots, dye molecules, and superconducting qubits can be accompanied by processes that do not change the system energy but break the phase coherence of oscillations. These processes are called dephasing or decoherence processes. In particular, they lead to the collisional broadening of the emission line of gases [1]. As shown in Sect. 3.2.4, the dephasing rate can exceed the energy dissipation rate by several orders of magnitude [2–5]. In these cases, $\gamma_\sigma > \gamma_D/2$ (see the discussion at the end of Sect. 3.2.4).

5.1 The Mollow Triplet

First, we start with the resonant case, in which the frequency of the external field is the same as the TLS transition frequency, $\Delta_\omega = \omega_{ext} - \omega_\sigma = 0$, and consider the interaction with the reservoir of free space modes with no dephasing, so that $\gamma_\sigma = \gamma_D/2 \equiv \gamma/2$ (see Eq. (3.2.50)). Though this is an idealization and describes experiments only qualitatively, it allows us, following Mollow's pioneering work [6], to determine the radiation spectrum analytically.

To calculate the scattering spectrum, we bring the Heisenberg-Langevin equations to the form that is convenient for using the quantum regression theorem. For this purpose, we use variables defined in Eq. (3.4.34), which, for convenience, are reproduced here:

$$\Delta\widehat{\sigma}_{H\ slow}(t) = \widehat{\sigma}_{H\ slow}(t) - \langle\widehat{\sigma}\rangle^{st}_{slow}\widehat{I},$$
$$\Delta\widehat{\sigma}^{\dagger}{}_{H\ slow}(t) = \widehat{\sigma}^{\dagger}{}_{H\ slow}(t) - \left\langle\widehat{\sigma}^{\dagger}\right\rangle^{st}_{slow}\widehat{I},$$
$$\Delta\widehat{D}_H(t) = \widehat{D}_H(t) - \left\langle\widehat{D}\right\rangle^{st}\widehat{I})$$

Further, to find the correlation functions, we should solve the system of differential equations Eq. (3.4.35)) in which, for $\Delta_\omega = \omega_{ext} - \omega_\sigma = 0$ and $\gamma_\sigma = \gamma/2$, the matrix $\mathbf{M}$ is replaced with

$$\mathbf{M} = \begin{pmatrix} -\gamma/2 & 0 & -i\Omega_{ext} \\ 0 & -\gamma/2 & i\Omega_{ext} \\ 2i\Omega_{ext} & -2i\Omega_{ext} & -\gamma \end{pmatrix}, \tag{5.1.2}$$

Now, the system of Eq. (3.4.35) can be solved analytically. The eigenvalues $\lambda_{1,\,2,\,3}$ of the transition matrix of Eq. (3.4.35) can be found by solving the cubic equation $\det\mathbf{M} = 0$:

$$\lambda_1 = -\gamma/2, \lambda_{2,3} = -3\gamma/4 \pm \frac{1}{4}\sqrt{\gamma^2 - 64\Omega_{ext}}. \tag{5.1.3}$$

The corresponding eigenvectors are

$$\mathbf{h}_1 = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \\ 0 \end{pmatrix}, \quad \mathbf{h}_{2,3} = \begin{pmatrix} -4i\Omega_{ext}/\left(\gamma \mp \sqrt{\gamma^2 - 64\Omega_{ext}^2}\right) \\ 4i\Omega/\left(\gamma \mp \sqrt{\gamma^2 - 64\Omega_{ext}^2}\right) \\ 1 \end{pmatrix}. \tag{5.1.4}$$

The solution to system (3.4.35) may be presented as

$$\begin{pmatrix} \left\langle \Delta\widehat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\widehat{\sigma}_{slow}(t_{st}) \right\rangle \\ \left\langle \Delta\widehat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\widehat{\sigma}^{\dagger}_{slow}(t_{st}) \right\rangle \\ \left\langle \Delta\widehat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\widehat{D}(t_{st}) \right\rangle \end{pmatrix} = c_1\mathbf{h}_1 \exp(\lambda_1\tau) + c_2\mathbf{h}_2 \exp(\lambda_2\tau) + c_3\mathbf{h}_3 \exp(\lambda_3\tau), \tag{5.1.5}$$

where the coefficients $c_{1,\,2,\,3}$ can be found by putting $\tau = 0$ and using Eqs. (3.4.36)–(3.4.38) (see Problem 1.13).

The final expression for the correlator $\left\langle \Delta\widehat{\sigma}^{\dagger}(t_{st}+\tau)\Delta\widehat{\sigma}(t_{st}) \right\rangle$ has the form:

$$\left\langle \Delta\widehat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\widehat{\sigma}_{slow}(t_{st}) \right\rangle = \frac{64\Omega_{ext}^2 \exp(-\gamma\tau/2)}{\gamma^2\left(1+64\Omega^2/\gamma^2\right)} \times \left[1 - \frac{1}{2\left(1+64\Omega_{ext}^2/\gamma^2\right)}\right.$$
$$\times \left(1 - \frac{64\Omega_{ext}^2}{\gamma^2} + \frac{1-40\Omega_{ext}^2/\gamma^2}{\sqrt{1-64\Omega_{ext}^2/\gamma^2}}\right) \exp\left(-\frac{\gamma}{4}\left(1-\sqrt{1-64\Omega_{ext}^2/\gamma^2}\right)\tau\right)$$
$$\left. - \frac{1}{2\left(1+64\Omega_{ext}^2/\gamma^2\right)}\left(1 - \frac{64\Omega_{ext}^2}{\gamma^2} - \frac{1-40\Omega_{ext}^2/\gamma^2}{\sqrt{1-64\Omega_{ext}^2/\gamma^2}}\right) \exp\left(-\frac{\gamma}{4}\left(1+\sqrt{1-64\Omega_{ext}^2/\gamma^2}\right)\tau\right)\right]. \tag{5.1.6}$$

For further analysis, it is convenient to present the correlation function in the form (3.4.39) and separate the spectrum into coherent and incoherent parts:

$$S(\omega) = S_{coh}(\omega) + S_{incoh}(\omega),$$
$$S_{coh}(\omega) = \frac{1}{\pi}\,\mathrm{Re}\int_0^{\infty} d\tau \left|\langle\widehat{\sigma}\rangle^{st}_{slow}\right|^2 \exp(-i(\omega-\omega_{ext})\tau),$$

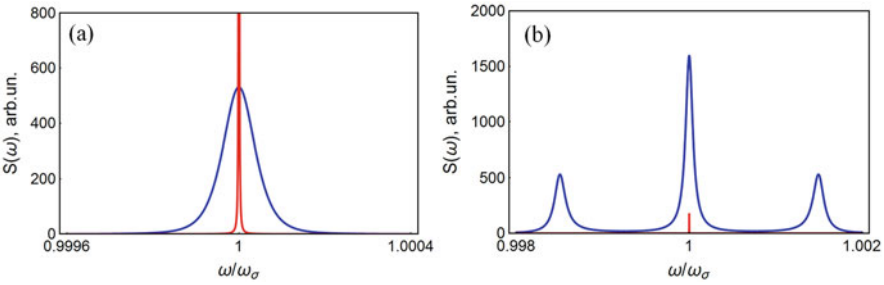

Fig. 5.1 The coherent S_{sr}^{coh} (the red line) and incoherent S_{sr}^{incoh} (the blue line) spectra of the TLS, $\gamma_\sigma = \gamma_D/2 = 0.5 \cdot 10^{-4}\omega_\sigma$ and $\omega_{ext} = \omega_\sigma$. (**a**) $\Omega_{ext} = 0.25\gamma_D$; (**b**) $\Omega_{ext} = 7.5\gamma_D$. The external field is assumed to have a finite coherence time $\tau_{coh} = 1/\gamma_{coh}$, $\gamma_{coh} = 10^{-3}\gamma_D$

$$S_{incoh}(\omega) = \frac{1}{\pi}\,\mathrm{Re}\int_0^\infty d\tau \left\langle \Delta\widehat{\sigma}^\dagger_{slow}(t_{st}+\tau)\Delta\widehat{\sigma}_{slow}(t_{st})\right\rangle \exp(-i(\omega-\omega_{ext})\tau).$$

If the Rabi frequency is small, $\Omega_{ext} \ll \gamma$, instead of the Rabi oscillations, we observe aperiodic evolution of the TLS, and the spontaneous emission spectrum has the form of a single Lorentz line (Fig. 5.1a).

When the Rabi frequency is high, $\Omega_{ext} \gg \gamma$, the spontaneous emission spectrum is incoherent, forming three Lorentz lines. Such spectrum is usually referred to as the Mollow triplet shown in Fig. 5.1b, by blue lines. Indeed, in this limit, we have:

$$S_{sr}^{incoh}(\omega) \sim \frac{\gamma/2}{(\gamma/2)^2 + (\omega-\omega_{ext})^2} + \frac{1}{2}\frac{3\gamma/4}{(3\gamma/4)^2 + (\omega-(\omega_{ext}-2\Omega_{ext}))^2} + \frac{1}{2}\frac{3\gamma/4}{(3\gamma/4)^2 + (\omega-(\omega_{ext}+2\Omega_{ext}))^2} \tag{5.1.7}$$

Note, that at $\gamma \to 0$, the spectrum is reduced to the sum of three delta-functions (see also Sect. 2.3).

In Fig. 5.1, coherent S_{sr}^{coh} and incoherent S_{sr}^{incoh} parts of the spectrum of the scattering radiation are shown by red and blue lines, respectively. The "graph" of a delta-function says nothing about its intensity. To make it easier to compare the contributions of S_{sr}^{coh} and S_{sr}^{incoh}, we suppose that the external field has a finite coherence time so that the δ-like Rayleigh peak is "smeared" over a small frequency range. As a result, the function $|\langle\widehat{\sigma}_{st}\rangle|^2\delta(\omega-\omega_{ext})$ is substituted with $\frac{|\langle\widehat{\sigma}_{st}\rangle|^2\gamma_{beam}/2}{(\gamma_{beam}/2)^2+(\omega-\omega_{ext})^2}$. In Figs. 5.1, 5.3, 5.4 and 5.5, we use $\gamma_{coh} = 10^{-3}\gamma_D$.

In the limit $\gamma/\Omega \to 0$, Eq. (5.1.6) is simplified and has the form:

$$\left\langle \Delta\widehat{\sigma}^{\dagger}_{slow}(t_{st}+\tau)\Delta\widehat{\sigma}_{slow}(t_{st})\right\rangle \simeq \frac{1}{4}\left(1+\frac{1}{2}\exp(-i2\Omega_{ext}\tau)+\frac{1}{2}\exp(i2\Omega_{ext}\tau)\right). \tag{5.1.8}$$

This equation coincides with Eq. (5.1.1) obtained for the non-dissipative Rabi problem. Note that such a response becomes coherent if $\gamma = 0$ and should be shown with additional red picks. For arbitrarily small γ, the response is incoherent and should be shown with blue lines.

It is worth emphasizing that the first term in Eq. (3.4.39) is responsible for the coherent elastic Rayleigh scattering at the frequency of the external field $\omega_{ext} = \omega_{\sigma}$.

In the limit $\gamma_{\sigma}/\Omega_{ext} \to 0$, the total intensity of the Rayleigh scattering (red line) is much less than the intensity of the Mollow triplet (blue lines). Indeed, the intensity of the Rayleigh scattering is proportional to $|\langle\widehat{\sigma}_{st}\rangle|^2$ (see Eq. (3.4.39)), which in the limit $\gamma_{\sigma}/\Omega_{ext} \to 0$ is proportional to $\left\langle\widehat{\sigma}^{\dagger}_{st}\right\rangle\langle\widehat{\sigma}_{st}\rangle \sim \gamma^2_{\sigma}/\Omega^2_{ext} \ll 1$ (see Eq. (3.4.33)). In turn, the intensity of the Mollow triplet is proportional to $\left\langle\Delta\widehat{\sigma}^{\dagger}(t_{st})\Delta\widehat{\sigma}(t_{st})\right\rangle$ (see Eq. (3.4.39)). In the limit $\gamma_{\sigma}/\Omega_{ext} \to 0$, $\left\langle\Delta\widehat{\sigma}^{\dagger}_{slow}(t_{st})\Delta\widehat{\sigma}_{slow}(t_{st})\right\rangle$ behaves as $\left\langle\widehat{\sigma}^{\dagger}(t_{st})\widehat{\sigma}(t_{st})\right\rangle = \left(1+\left\langle\widehat{D}(t_{st})\right\rangle\right)/2 \sim 1/2$ (see Eq. (3.4.33)). Thus, the sharp peak on the frequency ω_{ext}, in the Rayleigh spectrum, is a part of the Mollow triplet.

Let us consider the energies of the coherent W_{coh} (Rayleigh) and incoherent W_{incoh} (Mollow) parts of the spectrum. These energies are the areas under the lines S_{coh} and S_{incoh}, and they can be calculated directly:

$$W_{coh} = \int\limits_{-\infty}^{\infty} d\omega S_{coh}(\omega) = \left|\langle\widehat{\sigma}\rangle^{st}_{slow}\right|^2 \tag{5.1.9}$$

$$W_{incoh} = \int\limits_{-\infty}^{\infty} d\omega S_{incoh}(\omega) = \left\langle\Delta\widehat{\sigma}^{\dagger}_{slow}(t_{st})\Delta\widehat{\sigma}_{slow}(t_{st})\right\rangle \tag{5.1.10}$$

The values $\left|\langle\widehat{\sigma}\rangle^{st}_{slow}\right|^2$ and $\left\langle\Delta\widehat{\sigma}^{\dagger}_{slow}(t_{st})\Delta\widehat{\sigma}_{slow}(t_{st})\right\rangle$ are determined by Eqs. (3.4.33) and (3.4.36).

In Fig. 5.2, the dependencies of W_{coh} and W_{incoh} on the Rabi constant Ω_{ext} are shown. We see that for a small Rabi constant, the main part of the energy supplied by the external field belongs to coherent-driven oscillations of the TLS. For a large Rabi constant, the main energy contribution is due to the incoherent TLS oscillations, while the energy of the coherent Rayleigh response tends to zero.

In Fig. 5.2, the black points mark the values of W_{coh} and W_{incoh} at $\Omega_{ext} = 0.25\gamma_D$. These values, according to Eqs. (5.1.9)–(5.1.10), are equal to the areas under the red and blue curves in Fig. 5.1a. In this case, $W_{coh} > W_{incoh}$, while at $\Omega_{ext} = 7.5\gamma_D$, the green points in Fig. 5.2. the values of W_{coh} and W_{incoh} equal the areas under the red and blue curves in Fig. 5.1b and $W_{coh} < W_{incoh}$.

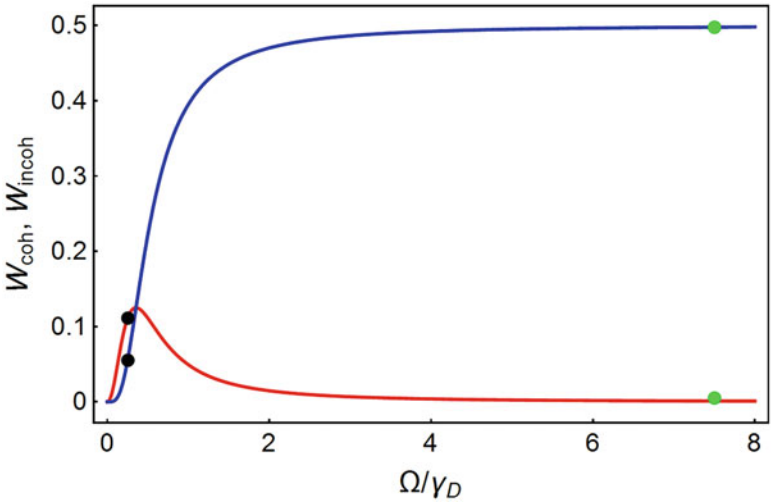

Fig. 5.2 The dependence of W_{coh} (the red line) and W_{incoh} (the blue line) on Ω_{ext}; $\gamma_\sigma = \gamma_D/2 = 0.5 \cdot 10^{-4}\omega_\sigma$ and $\omega_{ext} = \omega_\sigma$. Black points denote the values of W_{coh} and W_{incoh} at $\Omega_{ext} = 0.25\gamma_D$; green points denote the values of W_{coh} and W_{incoh} at $\Omega_{ext} = 7.5\gamma_D$

According to Eqs. (3.4.32) and (3.4.36), the incoherent contribution W_{incoh} increases at strong field, while W_{coh} decreases (see Fig. 5.2).

5.2 Beyond the Mollow Approximation

When dephasing is substantial, $\gamma_\sigma = \gamma_D/2 + \gamma_{deph} \gg \gamma_D/2$, or the scattering is not resonant, $\Delta_\omega = \omega_{ext} - \omega_\sigma \neq 0$, system (3.4.35) for correlator functions and, consequently, their Fourier spectra, Eq. (3.4.22), can only be analyzed numerically.

5.2.1 The Resonant Case with Dephasing

In this case, the matrix **M** in Eq. (5.1.2) changes to

$$\mathbf{M} = \begin{pmatrix} -\gamma_\sigma/2 & 0 & -i\Omega_{ext} \\ 0 & -\gamma_\sigma/2 & i\Omega_{ext} \\ 2i\Omega_{ext} & -2i\Omega_{ext} & -\gamma_D \end{pmatrix}$$

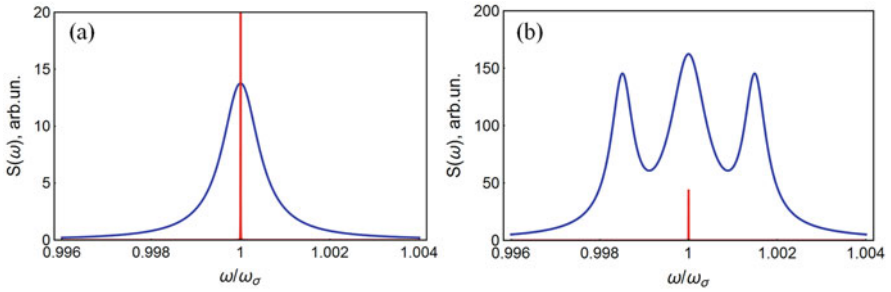

Fig. 5.3 The spectrum $S(\omega)$ of a TLS; $\gamma_\sigma = 2 \cdot 10^{-4}\omega_\sigma > \gamma_D/2$ and $\omega_{ext} = \omega_\sigma$. (**a**) $\Omega_{ext} = 0.25\gamma_D$; (**b**) $\Omega_{ext} = 7.5\gamma_D$

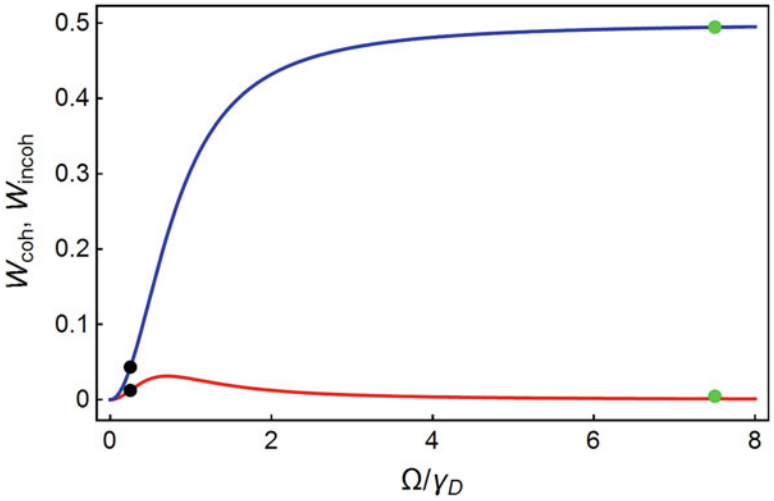

Fig. 5.4 The dependence of W_{coh} (the red line) and W_{incoh} (the blue line) on Ω_{ext}, $\gamma_\sigma = 2 \cdot 10^{-4}\omega_\sigma > \gamma_D/2$, and $\omega_{ext} = \omega_\sigma$. Black points denote the values of W_{coh} and W_{incoh} at $\Omega_{ext} = 0.25\gamma_D$; green points denote the values of W_{coh} and W_{incoh} at $\Omega_{ext} = 7.5\gamma_D$

The equation $\det \mathbf{M} = 0$ can only be solved numerically. The numerical analysis shows that the spectrum shape changes. In the resonant case, this change is only quantitative (compare Fig. 5.3a, b to Fig. 5.1a, b) – the linewidth is reduced from $\gamma_D/2$ to γ_σ.

In Fig. 5.4, the dependencies of W_{coh} and W_{incoh} on the Rabi constant Ω_{ext} are shown in the case of dephasing. For $\Omega_{ext} = 0.25\gamma_D$ and $\Omega_{ext} = 7.5\gamma_D$, the values of W_{coh} and W_{incoh} are shown by the black and green points. These values, according to Eqs. (5.1.9)–(5.1.10), are equal to the areas under the red and blue curves in Fig. 5.3a, b, respectively. Qualitatively, the behaviors of W_{coh} and W_{incoh} are the same as if there is no dephasing.

Thus, the dephasing reservoir lives up to its name: the interaction with it reduces the coherent response of the TLS.

5.2.2 *The Off-Resonant Case with Dephasing*

Now, we consider a nonresonant scattering, $\Delta_\omega \neq 0$, which has received much less attention in the literature. This case, however, corresponds to the most common experimental realization.

Once again, we emphasize that even when the frequency of the incident field differs from the TLS transition frequency, the dipole moment of the TLS performs harmonic oscillations precisely at the frequency of the incident field. Indeed, from Eq. (3.4.32), it follows that in the limit of large detuning Δ_ω, in the stationary regime ($\langle\widehat{\sigma}\rangle^{st} \neq 0$), we have:

$$\left|\left\langle\widehat{\mathbf{d}}\right\rangle\right| = \mathrm{Re}\left(d_{eg}\langle\widehat{\sigma}\rangle^{st}\right) = -\frac{\Omega_{ext}}{\Delta_\omega}\cos(\omega_{ext}t). \tag{5.2.1}$$

In other words, the dynamics of a TLS under the action of a coherent classical field is reduced to forced oscillations. There is no photon absorption or emission. Note that, now, the matrix $\mathbf{M}$ in Eq. (5.1.2) changes to

$$\mathbf{M} = \begin{pmatrix} i\Delta_\omega - \gamma_\sigma/2 & 0 & -i\Omega_{ext} \\ 0 & -i\Delta_\omega - \gamma_\sigma/2 & i\Omega_{ext} \\ 2i\Omega_{ext} & -2i\Omega_{ext} & -\gamma_D \end{pmatrix}$$

Let us consider the spectrum shape when the detuning is large, $\Delta_\omega \gg \gamma_\sigma, \gamma_D, \Omega_{ext}$, and the external field is weak, $\gamma_\sigma \gg \Omega_{ext}$. As shown in Sect. 2.4, the Rabi frequency of TLS oscillations in an external field is equal to $2\Omega_\Delta = 2\sqrt{\Omega_{ext}^2 + \Delta_\omega^2/4}$, which becomes $\Omega_\Delta \approx \Delta_\omega/2$ at large detuning. When the conditions of strong coupling, $|\Delta_\omega| \gg \gamma_\sigma, \gamma_D, \Omega_{ext}$, and $\Omega_\Delta \gg \gamma_\sigma$, are fulfilled, we can expect that the TLS radiation spectrum has three peaks at the frequencies ω_{ext} and $\omega_{ext} \pm 2\Omega_\Delta$. Since at $|\Delta_\omega| \gg \gamma_\sigma$, γ_D, Ω_{ext}, we have $\Omega_\Delta \approx \Delta_\omega/2$; then, the frequencies of these peaks equal ω_{ext}, $\omega_{ext} + \Delta = 2\omega_{ext} - \omega_\sigma$, $\omega_{ext} - \Delta_\omega = \omega_\sigma$. This is confirmed by computer simulation employing Eqs. (3.4.35) and (3.4.42). The results of the simulation are shown in Fig. 5.5.

The spectrum has three picks at ω_{ext} (the red line) and $\omega_{ext} \pm 2\Omega_\Delta \approx \omega_{ext} \pm \Delta_\omega$ (the blue lines). As shown in the previous subsection, the resonant Mollow triplet also has three peaks centered at the frequencies ω_{ext} and $\omega_{ext} \pm 2\Omega_{ext}$. Thus, when frequency detuning is large, we have a modified Mollow triplet. For $\gamma_\sigma = \gamma_D/2$, the graph of $S_{sr}(\omega)$ is shown in Fig. 5.5a. The linewidths of incoherent response (blue curves) are determined by $\gamma_D/2$. The red line represents the coherent Rayleigh scattering spectrum.

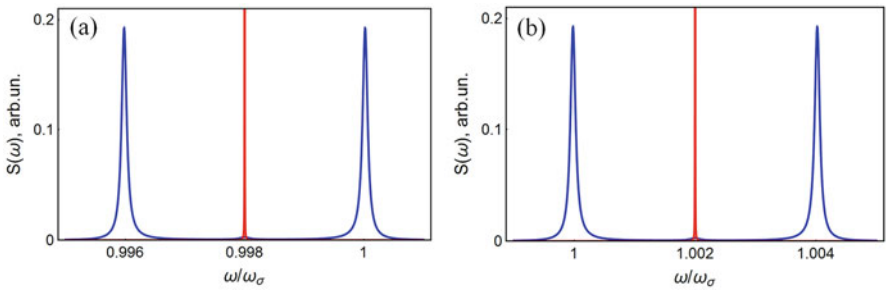

Fig. 5.5 The TLS spectrum $S(\omega)$ for $\Omega_{ext} = 1.5\gamma_D$, $\gamma_\sigma = \gamma_D/2 = 0.5 \cdot 10^{-4}\omega_\sigma$ (without dephasing) and small detuning (**a**) $\omega_{ext} - \omega_\sigma = -20\gamma_D \approx -0.002$, (**b**) $\omega_{ext} - \omega_\sigma = 20\gamma_D \approx 0.002$. The frequency ω_{ext} corresponds to the Rayleigh scattering shown by red lines

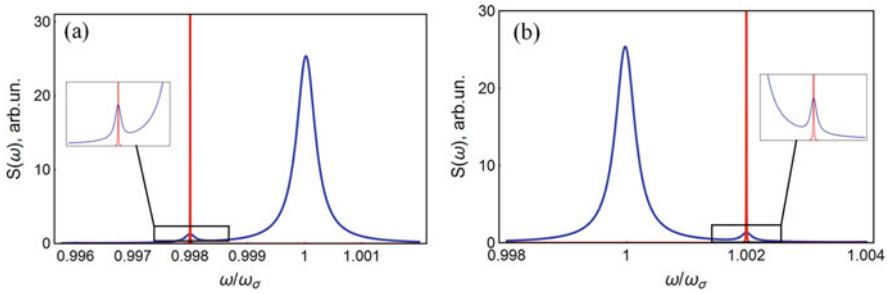

Fig. 5.6 The TLS spectrum $S_{sr}(\omega)$ for $\Omega_{ext} = 1.5\gamma_D$, $\gamma_\sigma = 2\gamma_D = 2 \cdot 10^{-4}\omega_\sigma$ (the same case as in Fig. 5.5 but with dephasing) (**a**) $\omega_{ext} - \omega_\sigma = -20\gamma_D$, (**b**) $\omega_{ext} - \omega_\sigma = 20\gamma_D$

For $\gamma_\sigma \gg \gamma_D/2$ ($\gamma_{deph} \neq 0$), the spectrum becomes nonsymmetric (see Fig. 5.6). The maximal amplitude of the spectrum is achieved at $\omega = \omega_\sigma$, while the other lines are suppressed.

Figure 5.7 shows the dependencies of W_{coh} and W_{incoh} on the rate γ_σ at fixed $\Omega_{ext} = 1.5\gamma_D$ and $\omega_{ext} = \omega_\sigma + 20\gamma_\sigma$. The black and green points denote the values of W_{coh} and W_{incoh} at $\gamma_\sigma = \gamma_D/2$ (no dephasing) and $\gamma_\sigma = 2\gamma_D$ (high dephasing), respectively. These values are equal to the areas under the red and blue curves in Figs. 5.5 and 5.6, respectively. One can see that the incoherent part of the energy W_{incoh} increases with an increase in dephasing. For this reason, the amplitude of the incoherent part of the spectrum in the case of dephasing is larger than without dephasing (see amplitudes of blue lines in Figs. 5.5 and 5.6).

The off-resonant scattering, $|\omega_{ext} - \omega_\sigma| \ll \omega_\sigma$, and the high dephasing rate, $\gamma_\sigma \gg \gamma_D/2$, are usually realized in experiments in which light scatters on molecules. Therefore, the form of the spontaneous emission spectrum is close to a single Lorentz line at the atom transition frequency (see Fig. 5.6) with a linewidth of about γ_σ. Near the frequency of Rayleigh scattering ω_{ext}, the spectrum has a

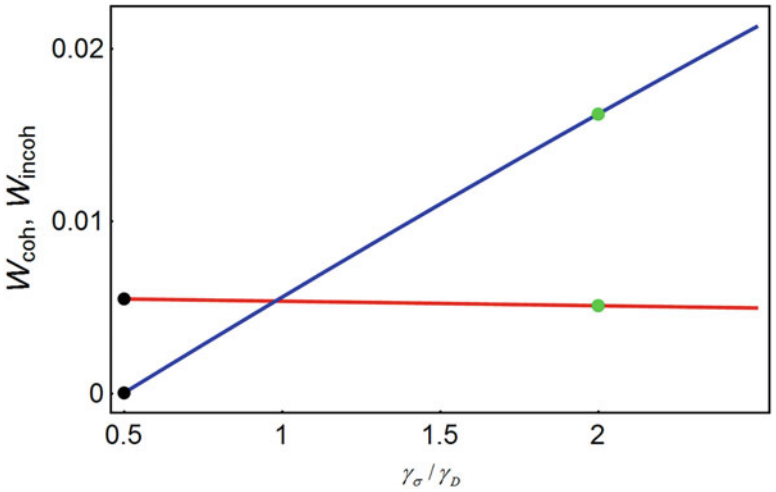

Fig. 5.7 The dependence of W_{coh} (the red line) and W_{incoh} (the blue line) on the dephasing, γ_σ/γ_D and $\Omega_{ext} = 0.5\gamma_D$, $\omega_{ext} = \omega_\sigma + 20\gamma_D$. Black and green points denote the values of W_{coh} and W_{incoh} at $\gamma_\sigma/\gamma_D = 0.5$ and $\gamma_\sigma/\gamma_D = 2.0$

background due to luminescence at the atom transition frequency and a weak peak due to spontaneous emission at the external field frequency. However, the ratio of the amplitude of this peak to the background tends to zero at large detuning (Fig. 5.5). By using numerical analysis, one can show that the amplitude of the background is of the order of $\Omega_{ext}^2\gamma_\sigma^2/\Delta_\omega^4$, and the linewidths of two latter peaks are smaller than γ_σ.

Remark 5.1 **Background spectrum in experiments on off-resonant Raman scattering** In the second part of the book, we discuss the spectrum of spontaneous Raman scattering. We demonstrate that Raman scattering arises from the modulation of coherent oscillations of the TLS dipole moment by incoherent oscillations of nuclei. These coherent oscillations are initiated during Rayleigh scattering. In experiment, the Raman spectrum manifests as peaks against a background (see Ref. [7]). This background stems from the low-frequency wing of the incoherent Mollow triplet. This background does not interfere with the formation of the Raman spectrum. In experiment, the background is automatically accounted for and subtracted from the total spectrum.

To summarize, in the limit $\Delta_\omega \gg \gamma_\sigma \gg \Omega_{ext}$, in the radiation spectrum near the external field frequency, there is a δ-peak of Rayleigh scattering and the background from the spontaneous emission at the atomic transition frequency.

We have shown that the quantum consideration of the scattering of an EM wave by a TLS explains both the coherent Rayleigh response at the frequency of the external field and the incoherent spontaneous emission, which has the form of the Mollow triplet. Note that when the frequencies of the external field and the TLS transition are different, the intensity in the Mollow triplet is distributed in such a way that it has a maximum at the transition frequency of the atom. Often, this maximum is associated with fluorescence (see Remark 5.1).

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Chapter 6
Quantum Description of Rayleigh Scattering of Quantized Electromagnetic Field

In this chapter, we study the scattering of photons belonging to a selected free space mode by a quantum atom. Below, we refer to the selected mode as incident mode. We assume that the frequency of the incident wave is incommensurable with any frequency of inter-level atomic transitions. We model the atom as a TLS with the transition frequency ω_σ. All free space modes except the selected mode are considered to be a thermalized reservoir having zero temperature. This implies that such EM field modes are empty.

We consider a quantum system, one part of which consists of an atom and a selected mode, and the other part is the reservoir of free space modes (the Hermitian properties of these parts are discussed in Sect. 2.2). The eigenstates of the first part are entangled states of the atom and incident photons. Such a system is often called a dressed atom. These states are generalizations of the Jaynes-Cummings states for the quantized incident light. The two parts are coupled via the interaction of the atom with both the modes of the reservoir and photons of incident mode.

The scattering process is considered to be the spontaneous emission of the photons of the incident mode into the reservoir of free space modes. Additional excitations of the reservoir modes, which arise during the relaxation, are treated as scattered light. Such a consideration corresponds to experiments in which the incident field has a narrow frequency spectrum, as in lasers.

6.1 The Lindblad Equation for Rayleigh Scattering

We solve the scattering problem in two steps. First, we consider the subsystem of a TLS interacting with an incident EM mode, which contains n_0 quanta. In the next step, we consider the evolving in time dipole moment of the atom as a cause for the perturbation of the reservoir of free space modes. It is the excitation of free space modes that is treated as scattering.

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The first step is the Jaynes-Cummings problem, the solution to which has been discussed in Sect. 2.5. Thus, after the first step, the problem is reduced to the spontaneous relaxation of the Jaynes-Cummings solution.

Now, we focus on the second step. The Hamiltonian of free space modes and the Hamiltonian of interaction of the considered system with these modes have the forms (3.1.2) and (3.1.3), respectively. Note that only the atom interacts with the free space modes, therefore, the interaction Hamiltonian of the considered system with the reservoir is the same as for a single atom in free space (see Sect. 3.1).

Below, to describe the relaxation of the subsystem, we follow the general procedure developed in Sect. 3.2. Recall that to derive the Lindblad master equation, one has to expand the operator of the interaction between the system and the reservoir over the system eigenstates (see Eq. (3.2.26)). The atom interacts with the reservoir via its dipole moment determined by the operators $\widehat{S}=\widehat{\sigma}$ and $\widehat{\sigma}^{\dagger}$ (see interaction Hamiltonian (3.1.3)). The system eigenstates are the Jaynes-Cummings eigenstates described by Eqs. (2.5.34) and (2.5.36). These eigenstates comprise a complete basis $\{|k\rangle\} = \{|g,0\rangle, |-,n\rangle, |+,n\rangle\}$ of the system states in the corresponding Jaynes-Cummings Hilbert space. Similarly to the TLS Hilbert space, where the basis for operators is formed by the transition operators, using the Jaynes-Cummings eigenstates for the basis of Jaynes-Cummings Hilbert space, one can form a basis for operators from the transition operators $\widehat{S}_{k'k''}=|k'\rangle\langle k''|$ (see Eqs. (2.2.5) and (3.2.25)).

One can show (see Problem 1.19) that the operator $\widehat{\sigma}$ can be represented in terms of the following set of transition operators:

$$\begin{aligned}
&\widehat{S}_{1,n}=|+,n-1\rangle\langle+,n|,\ \ \widehat{S}_{2,n}=|+,n-1\rangle\langle-,n|,\ \ \widehat{S}_{3,n}=|-,n-1\rangle\langle+,n|,\\
&\widehat{S}_{4,n}=|-,n-1\rangle\langle-,n|,\quad \widehat{S}_{2,1}=|g,0\rangle\langle-,1|,\ \ \widehat{S}_{1,1}=|g,0\rangle\langle+,1|,\\
&\widehat{S}_{1,0}=\widehat{S}_{3,0}=\widehat{S}_{4,0}=0
\end{aligned} \tag{6.1.1}$$

Thus,

$$\begin{aligned}
\widehat{\sigma} = \cos\varphi_1\widehat{S}_{1,1} - \sin\varphi_1\widehat{S}_{2,1} + \sum_{n=1}^{\infty}\Big(&\cos\varphi_n\sin\varphi_{n-1}\widehat{S}_{1,n}\\
&- \sin\varphi_n\sin\varphi_{n-1}\widehat{S}_{2,n} + \cos\varphi_n\cos\varphi_{n-1}\widehat{S}_{3,n} - \sin\varphi_n\cos\varphi_{n-1}\widehat{S}_{4,n}\Big),
\end{aligned} \tag{6.1.2}$$

where $\tan(2\varphi_n)=2\Omega_a\sqrt{n}/|\Delta_a|$. Using expansion (6.1.2), we can write the Hamiltonian $\widehat{H}_{\mathrm{SR}}$ described by Eq. (3.1.3):

$$\widehat{H}_{\mathrm{SR}} = \sum_{k,\lambda} \hbar\Omega_{k,\lambda} a^{\dagger}_{k,\lambda} (\cos\varphi_1 \widehat{S}_{1,1} - \sin\varphi_1 \widehat{S}_{2,1} + \infty \sum_{n=1} \Big(\cos\varphi_n \sin\varphi_{n-1} \widehat{S}_{1,n} - \sin\varphi_n \sin\varphi_{n-1} \widehat{S}_{2,n} + \cos\varphi_n \cos\varphi_{n-1} \widehat{S}_{3,n} - \sin\varphi_n \cos\varphi_{n-1} \widehat{S}_{4,n} \Big)) + h.c. \tag{6.1.3}$$

Knowing the Jaynes-Cummings-eigenstates, we can exclude free space mode variables except for the selected mode. Since we deal with optical frequencies, we may neglect relativistic effects. Following the standard procedure (see Sect. 3.2.),[1] we can exclude the reservoir variables and obtain the Lindblad master Eq. [1–3] for the system density matrix. In basis (6.1.1), the equation looks as (see Problem 1.20)

$$\begin{aligned}
\frac{\partial\widehat{\rho}}{\partial t} = {} & \frac{i}{\hbar}\left[\widehat{\rho}, \widehat{H}_{\mathrm{S}}\right] \\
& + \frac{\gamma_{1,1}}{2} \cos^2\varphi_1 \left(2\widehat{S}_{1,1}\widehat{\rho}\widehat{S}^{\dagger}_{1,1} - \widehat{S}^{\dagger}_{1,1}\widehat{S}_{1,1}\widehat{\rho} - \widehat{\rho}\widehat{S}^{\dagger}_{1,1}\widehat{S}_{1,1} \right) \\
& + \frac{\gamma_{2,1}}{2} \sin^2\varphi_1 \left(2\widehat{S}_{2,1}\widehat{\rho}\widehat{S}^{\dagger}_{2,1} - \widehat{S}^{\dagger}_{2,1}\widehat{S}_{2,1}\widehat{\rho} - \widehat{\rho}\widehat{S}^{\dagger}_{2,1}\widehat{S}_{2,1} \right) \\
& + \infty \sum_{n=2} \Big(\frac{\gamma_{1,n}}{2} \cos^2\varphi_n \sin^2\varphi_{n-1} \left(2\widehat{S}_{1,n}\widehat{\rho}\widehat{S}^{\dagger}_{1,n} - \widehat{S}^{\dagger}_{1,n}\widehat{S}_{1,n}\widehat{\rho} - \widehat{\rho}\widehat{S}^{\dagger}_{1,n}\widehat{S}_{1,n} \right) \\
& + \frac{\gamma_{2,n}}{2} \sin^2\varphi_n \sin^2\varphi_{n-1} \left(2\widehat{S}_{2,n}\widehat{\rho}\widehat{S}^{\dagger}_{2,n} - \widehat{S}^{\dagger}_{2,n}\widehat{S}_{2,n}\widehat{\rho} - \widehat{\rho}\widehat{S}^{\dagger}_{2,n}\widehat{S}_{2,n} \right) \\
& + \frac{\gamma_{3,n}}{2} \cos^2\varphi_n \cos^2\varphi_{n-1} \left(2\widehat{S}_{3,n}\widehat{\rho}\widehat{S}^{\dagger}_{3,n} - \widehat{S}^{\dagger}_{3,n}\widehat{S}_{3,n}\widehat{\rho} - \widehat{\rho}\widehat{S}^{\dagger}_{3,n}\widehat{S}_{3,n} \right) \\
& + \frac{\gamma_{4,n}}{2} \sin^2\varphi_n \cos^2\varphi_{n-1} \left(2\widehat{S}_{4,n}\widehat{\rho}\widehat{S}^{\dagger}_{4,n} - \widehat{S}^{\dagger}_{4,n}\widehat{S}_{4,n}\widehat{\rho} - \widehat{\rho}\widehat{S}^{\dagger}_{4,n}\widehat{S}_{4,n} \right) \Big).
\end{aligned} \tag{6.1.4}$$

Here $S_{i,\,n}$ are the transition operators between the Jaynes-Cummings eigenstates, determined by Eq. (6.1.1) and

$$\gamma_{1,1} = \gamma_D^{(rad)} \frac{\omega^3_{+,1}}{\omega^3_{\sigma}}, \quad \gamma_{2,1} = \gamma_D^{(rad)} \frac{\omega^3_{-,1}}{\omega^3_{\sigma}}, \quad \gamma_{1,n} = \gamma_D^{(rad)} \frac{(\omega_{+,n+1} - \omega_{+,n})^3}{\omega^3_{\sigma}},$$
$$\gamma_{2,n} = \gamma_D^{(rad)} \frac{(\omega_{-,n+1} - \omega_{-,n})^3}{\omega^3_{\sigma}}, \quad \gamma_{3,n} = \gamma_D^{(rad)} \frac{(\omega_{-,n-1} - \omega_{+,n})^3}{\omega^3_{\sigma}}, \quad \gamma_{4,n} = \gamma_D^{(rad)} \frac{(\omega_{-,n-1} - \omega_{-,n})^3}{\omega^3_{\sigma}} \tag{6.1.5}$$

Recall that the dissipation rate between eigenstates is determined by the frequency difference between eigenstates (see Remark 3.3). For this reason, the rates in Lindblad equation (6.1.4) differ from the radiation rate of a TLS in free space by the factor $(\omega_{\pm,n+1} - \omega_{\pm,n})^3/\omega^3_{\sigma}$ (see Problem 1.20).

[1] It is important to note that the frequency of the scattered photon changes by ω_{ext}. In the expression for γ_D, the density of states at the frequency of the emitted photon is included as a factor. This differs from the Rayleigh scattering, in which the scattering frequency is not ω_{σ}, but ω_{ext}, as in the case of spontaneous radiation.

Equation (6.1.4) is obtained after averaging the Hamiltonian $\widehat{H}_{\mathrm{SR}}$ over degrees of freedom of the reservoir. This is rather cumbersome but has a clear physical interpretation. Specifically, each term in Eq. (6.1.4) having $2\widehat{S}\widehat{\rho}\widehat{S}^{\dagger} - \widehat{S}^{\dagger}\widehat{S}\widehat{\rho} - \widehat{\rho}\widehat{S}^{\dagger}\widehat{S}$ as a factor describes the system transitions between the eigenstates $\{|g,0\rangle, |+,\mathrm{n}\rangle, |-,\mathrm{n}\rangle\}$, $n = 1, 2, \ldots$. The explicit form of the $\widehat{S}$-operators is given by Eq. (6.1.1). We emphasize again that it is the interaction of the Jaynes-Cummings system with the reservoir of free space modes that leads to a transition between the eigenstates of this subsystem (see Problem 1.21).

Rayleigh scattering is not resonant; therefore, for simplicity, we consider a large frequency difference, $|\omega_\sigma - \omega_a| = |\Delta_a| \gg \Omega_a\sqrt{n}$, and a large resonator volume, $V \to \infty$. For definiteness, we assume that $\omega_a < \omega_\sigma$. In this limit, $\varphi_n \simeq \Omega_a\sqrt{n}/|\Delta_a|$, $\sin\varphi_n \simeq \varphi_n \simeq \Omega_a\sqrt{n}/|\Delta_a|$, and $\cos\varphi_n \simeq 1$, and the expression for eigenfrequencies (2.5.33) and eigenstates (2.5.34) could be expanded over the small parameter $\Omega_a\sqrt{n}/\Delta_a$:

$$\omega_{-,n} \approx n\omega_a - \Omega_a^2 n/|\Delta_a|, \qquad |-,n\rangle \approx -\frac{\Omega_a\sqrt{n}}{|\Delta_a|}|e,n-1\rangle + |g,n\rangle, \tag{6.1.6}$$

$$\omega_{+,n} \approx (n-1)\omega_a + \omega_\sigma + \Omega_a^2 n/|\Delta_a|, \qquad |+,n\rangle \approx |e,n-1\rangle + \frac{\Omega_a\sqrt{n}}{|\Delta_a|}|g,n\rangle. \tag{6.1.7}$$

One can see that in the limit $\Delta_a \gg \Omega_a\sqrt{n}$, the eigenfrequencies $\omega_{-,n}$ (see Eq. (6.1.6)) coincide with the eigenfrequencies $n\omega_a$ of the selected mode with the accuracy $\Omega_a^2 n/|\Delta_a|^2 \ll 1$, and the difference between the frequencies of the levels $|-,n\rangle$ and $|-,n+1\rangle$ is equal to $\omega_a - \Omega_a^2/|\Delta_a|$, which coincides with the frequency of the selected mode ω_a.

Since the transitions occur due to the interaction with the reservoir of free space modes, and the temperature is assumed to be zero, only transitions with a decrease in energy may occur. Thus, we may expect that a photon with a frequency ω_a is emitted during the transition between eigenstates $|-,n\rangle$ and $|-,n-1\rangle$. In this consideration, the states with the transition frequency ω_a arise naturally, and there is no need to introduce an additional virtual level.

It can be shown (see Eq. (22.3) in Problem 1.22) that in the limit $|\Delta_a| = |\omega_a - \omega_\sigma| \gg \Omega_a\sqrt{n}$ and for the initial condition $\widehat{\rho}(0) = |g,n_0\rangle\langle g,n_0|$, only the states $|-,n\rangle = -\sin\varphi_n|e,n-1\rangle + \cos\varphi_n|g,n\rangle$ with $n < n_0$ are mainly occupied.

Let us denote the diagonal elements as $p_n(t) = \langle -,n|\widehat{\rho}(t)|-,n\rangle$ and $\gamma_n \equiv \gamma_D^{(rad)}\Omega_a^2 n/|\Delta_a|^2$. In the limit $\Delta_a \gg \Omega_a\sqrt{n}$, the system of equations for $p_n(t)$ can be simplified (see Problem 1.22 and Sects. 3.2.2. and 3.2.3):

$$\begin{aligned}
\frac{dp_{n_0}(t)}{dt} &= -\gamma_{n_0} p_{n_0} \\
\frac{dp_n(t)}{dt} &= -\gamma_n p_n(t) + \gamma_{n+1} p_{n+1}(t), \qquad 1 \le n < n_0 \\
\frac{dp_0(t)}{dt} &= \gamma_1 p_1(t)
\end{aligned} \tag{6.1.8}$$

with the initial condition

$$p_{n_0}(0) = 1, p_n(0) = 0, 0 \le n < n_0. \tag{6.1.9}$$

The quantities $p_n(t)$ are obtained under assumption $\Omega_a^2 n/|\Delta_a|^2 \ll 1$ and have the meaning of the probabilities of the occupation of the entangled state of the selected mode and the atom $|-, n\rangle$; $\gamma_n \equiv \gamma_D^{(rad)} \Omega_a^2 n/|\Delta_a|^2$ has the meaning of the transition rate from the state $|-, n\rangle$ to the state $|-, n-1\rangle$.

As shown in Problem 1.22, the off-diagonal elements are $\Omega_a^2 n/|\Delta_a|^2 \ll 1$ times smaller than diagonal elements, and the density matrix $\rho(t) \equiv \widehat{P}_L(t;0)[\rho_S(0)]$ can be written as $\sum_n p_n(t)|-, n\rangle\langle -, n|$. Therefore, we disregard the off-diagonal elements in further calculations of the spectrum of emitted light.

As was mentioned, the spectrum of the system oscillation $S(\omega)$ is the Fourier transform of the two-time correlation function of system dynamic variables. For example, in the dipole approximation, to calculate the radiation spectrum of a TLS, we need to know the correlator $\langle \widehat{\sigma}_H(t+\tau)\widehat{\sigma}_H(t)\rangle$ (see Eq. (3.2.61)). Using Eqs. (6.1.4)–(6.1.9), one can show that in the Schrödinger picture, the two-time correlation function can be expressed as (see Problem 1.23)

$$\left\langle \widehat{\sigma}^{\dagger}(t+\tau)\widehat{\sigma}(t) \right\rangle \simeq \sum_{k=n_0}^{1} \left(\Omega_a^2 k/|\Delta_a|^2 \right) p_k(t) \exp((i\omega_a - (\gamma_k + \gamma_{k-1})/2)\tau). \tag{6.1.10}$$

Thus, we have described the algorithm for calculating the spectrum of the Rayleigh scattering. For this purpose, we consider scattering as a relaxation of an interacting atom and a photon from the selected mode to the reservoir of the other free space modes. We obtain the master equation for the system dynamics (Eq. (6.1.4)) and simplify this equation when the difference between the frequency of the selected mode and the atomic transition frequency is large (Eq. (6.1.8)). Note that all frequencies of the Jaynes-Cummings levels, determined by Eq. (2.5.33), correspond to real system frequencies, and there is no need to introduce a virtual level.

6.2 Rayleigh Scattering of Quantized Fields: Various Problem Statements

In this section, we discuss elastic photon scattering considered by Placzek [4], Berestetskii-Lifshitz-Pitaevskii [5], and Glauber [6]. Below, we show that the model of a dressed atom interacting with the reservoir of free space modes reproduces the elasticity of the Rayleigh scattering, and if the initial state of a photon from the selected mode is coherent, it yields the same results as the theory in which an incident photon is described as a classical field.

Strictly speaking, to solve the problem of scattering of N photons, it is necessary to solve system of Eqs. (6.1.8) which takes into account the transitions between all Jaynes-Cummings eigenstates (6.1.6). However, usually, we only need to consider a transition in which the number of photons in the selected mode changes by one. We do this in this section within the framework of the theory developed above.

We consider four specific cases of the scattering problem distinguished by initial conditions. First, we discuss the initial condition with one photon in the selected mode. This case corresponds to the Berestetskii-Lifshitz-Pitaevskii approach. This approach assumes that the scattering is a two-step process. In the first step, the atom absorbs a photon; in the second step, it radiates a photon back into free space. We demonstrate that even in this case, there is no photon absorption but only damped Rabi oscillations. This case is difficult to realize in experiment, and we only discuss it to clarify the physics of the phenomenon.

Second, we study a more realistic situation with n_0 incident photons and the transition to the state with $n_0 - 1$ photons in the selected mode. This case corresponds to Placzek's formulation of the problem. We show that, in this case, a narrow spectral line arises. However, to solve the problem of scattering of n_0 photons, it is necessary to solve system of Eq. (6.1.8), which takes into account the transitions between all eigenstates (6.1.6).

In the third example, we consider the scattering of n_0 photons, taking into account a cascade of transitions between the Jaynes-Cummings states. We show that this case reproduces almost all experimental features of Rayleigh scattering, including the narrow spectral line and the quasistationary occupancy of the atom states. However, the dipole moment of the atom is zero.

Finally, to reproduce a coherent response of the atom with a nonzero dipole moment, we consider the case of a coherent initial state of the selected mode. We obtain both a narrow spectral line and a nonzero quasistationary dipole moment of the atom.

6.2.1 Single-Photon Scattering: The Berestetskii-Lifshitz-Pitaevskii Formulation

First, we assume that initially, in the selected mode, only one photon is present, i.e., the initial condition is $n_0 = 1$. Such a setting was considered by Berestetskii, Lifshitz, and Pitaevskii [5] as a physical model for Rayleigh scattering. In this subsection, we show that single-photon scattering differs from classical Rayleigh scattering.

As mentioned in Sect. 2.3, in a system consisting of an atom and a photon, without the interaction with the reservoir, the atom's probability of being excited is $\left\langle \widehat{\sigma}^{\dagger}(t)\widehat{\sigma}(t) \right\rangle = p_e$, and the mean number of photons is $n_{\mathrm{ph}}(t) \equiv \left\langle \widehat{a}^{\dagger}(t)\widehat{a}(t) \right\rangle$. Such a system exhibits Rabi oscillations.

Our computer simulation shows that due to the interaction of the system with the reservoir of free space modes, both $p_e(t)$ and $n_{\mathrm{ph}}(t)$ become small compared to the background of the Rabi oscillations (see Fig. 6.1). These terms, therefore, vanish from Eq. (6.1.8). From the numerical simulation, we conclude that there are two characteristic times in the system dynamics – $\left(\gamma_D^{(rad)}\right)^{-1}$ and $\left(\gamma_D^{(rad)}\Omega_a^2/|\Delta_a|^2\right)^{-1}$.

From Fig. 6.1, we can see that initially, for $t \leq \left(\gamma_D^{(rad)}\right)^{-1}$, both $p_e(t)$ and $n_{\mathrm{ph}}(t)$ oscillate with the Rabi frequency $2\sqrt{\Omega_a^2 + (\Delta_a/2)^2}$. The Rabi oscillations of both quantities dissipate with the characteristic rate γ_D. The presence of the Rabi oscillations means that the photon from the selected mode is not absorbed.

After the dissipation of the Rabi oscillations, the probability of the atom being in the excited state reaches the value $\left(\Omega_a^2/|\Delta_a|^2\right)$. At the time $t \gg \gamma_0^{-1}$, $p_0(t)$ and $p_1(t)$ obey Eq. (6.1.8):

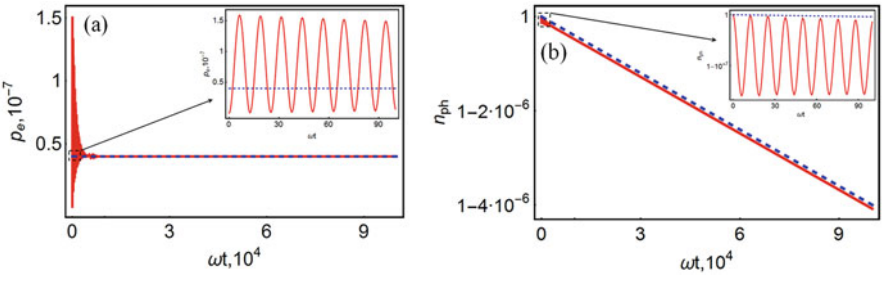

Fig. 6.1 Time dependence of (**a**) the probability of the atom to be in the excited state; (**b**) the number of photons in the selected mode

$$\begin{aligned}\frac{dp_1(t)}{dt} &= -\gamma_1 p_1(t),\\ \frac{dp_0(t)}{dt} &= \gamma_1 p_1(t),\end{aligned} \tag{6.2.1}$$

which solution has the form

$$p_1(t) = \exp\left(-\gamma_D^{(rad)}\left(\Omega_a^2/|\Delta_a|^2\right)t\right). \tag{6.2.2}$$

Using Eqs. (6.2.2) and (6.1.10), we find the solution to the expectation value of the population inversion $\left\langle \widehat{\sigma}^\dagger(t)\widehat{\sigma}(t)\right\rangle$:

$$\left\langle \widehat{\sigma}^\dagger(t)\widehat{\sigma}(t)\right\rangle = \left(\Omega_a^2 k/|\Delta_a|^2\right)p_1(t) \simeq \left(\Omega_a^2/|\Delta_a|^2\right)\exp\left(-\gamma_D^{(rad)}\left(\Omega_a^2/|\Delta_a|^2\right)t\right) \equiv p_e(t). \tag{6.2.3}$$

Equation (6.2.3) shows that the atom radiates with the rate $\gamma_D^{(rad)}\left(\Omega_a^2/|\Delta_a|^2\right)$. The initial excitation energy of the atom is $\Omega_a^2/|\Delta_a|^2$. Usually, in problems dealing with an atom in free space, the infinite volume limit is considered. In this limit, the coupling constant approaches zero as $\Omega_a \sim 1/\sqrt{V} \to 0$, and the radiation rate is infinitesimally small. Then, two-time correlation function (6.1.10) has the form:

$$\left\langle \widehat{\sigma}^\dagger(t+\tau)\widehat{\sigma}(t)\right\rangle \simeq \exp(i\omega_a\tau)\Omega_a^2/|\Delta_a|^2 \exp\left(-\gamma_D^{(rad)}\left(\Omega_a^2/|\Delta_a|^2\right)t\right)\exp\left(-\gamma_D^{(rad)}\left(\Omega_a^2/2|\Delta_a|^2\right)\tau\right). \tag{6.2.4}$$

Note that if we fix the time and find the spectrum as the Fourier transform of the two-time correlation function with respect to τ, then instead of the Rayleigh delta-function, we obtain a Lorentz line that is centered at the frequency ω_a and has a small linewidth $\sim \gamma_D^{(rad)}\left(\Omega_a^2/2|\Delta_a|^2\right) \ll \gamma_D^{(rad)}$.

Thus, when the system is far from the resonance, $|\omega_\sigma - \omega_a| = |\Delta_a| \gg \Omega_a\sqrt{n}$, the single-photon scattering is not elastic. The scattering spectrum has a narrow emission line. However, this narrow line corresponds to extremely slow radiation. Further, the total detectable energy emitted by the atom is $\sim \Omega_a^2/|\Delta_a|^2$, i.e., in the limit considered, it is also extremely small.

We have shown that in the case of one incident photon, this photon is not absorbed by the atom. Namely, instead of photon absorption, at the initial stage of the scattering, the Rabi oscillations of both excited state population and photon number occur because the initial state $|g,1\rangle$ is not the Jaynes-Cummings eigenstate. On expending $|g,1\rangle$ in the sum of Jaynes-Cummings, the states $|-,1\rangle$ and $|+,1\rangle$ arise. The Rabi oscillations are described by the off-diagonal element of the

corresponding density matrix $\rho_{(-,1)(+,1)}$. This element relaxes with time (see Problem 1.20). After the density matrix $\rho_{(-,1)(+,1)}$ relaxes, the system mainly occurs in the state $|-,1\rangle$. This state has a nonzero dipole transition with the ground state and can radiate interacting with the reservoir of free space modes. However, because the Rabi frequency tends to zero as $1/\sqrt{V}$, the time of radiation in the limit $V \to \infty$ tends to infinity. This contradicts experiments where the scattering process happens during a finite time. In the next subsection, we see that this discrepancy can be fixed if one considers the scattering of many photons.

6.2.2 Placzek's Approach

In the approach developed by Placzek, a single transition process in which the number of photons is changed by unity is considered. To reproduce the result of this approach, in system (6.1.8) we need to retain only one equation that describes the dynamics of the initial state $|-,n_0\rangle$. We assume that the initial state of the system is $p_{n_0}(0)=1$. Other states are assumed to be empty all the time, i.e., for $1 \le n < n_0$ $p_n(0)=p_n(t)=0$,. After such simplification, the system of Eq. (6.1.8) reduces to

$$\frac{d}{dt}p_{n_0}(t) = -\gamma_{n_0}p_{n_0} \tag{6.2.5}$$

The solution to this equation is $p_{n_0}(t)=\exp\left(-\gamma_{n_0}t\right)$. Using Eq. (6.1.10), for the population of the excited state of the atom, we obtain:

$$\left\langle \widehat{\sigma}^{\dagger}(t)\widehat{\sigma}(t)\right\rangle \simeq \left(\Omega_a^2 n/|\Delta_a|^2\right)\exp\left(-\gamma_D^{(rad)}\left(\Omega_a^2 n/|\Delta_a|^2\right)t\right). \tag{6.2.6}$$

For the two-time correlation function, we have:

$$\left\langle \widehat{\sigma}^{\dagger}(t+\tau)\widehat{\sigma}(t)\right\rangle \simeq \exp(i\omega_a\tau)\frac{\Omega_a^2 n}{|\Delta_a|^2}\exp\left(-\gamma_D^{(rad)}\left(\frac{\Omega_a^2 n}{|\Delta_a|^2}\right)t\right)\exp\left(-\gamma_D^{(rad)}\left(\frac{\Omega_a^2 n}{2|\Delta_a|^2}\right)\tau\right). \tag{6.2.7}$$

If we fix the time and make the Fourier transform of Eq. (6.2.7) on τ, we obtain the Lorentzian line with the width $\gamma_D^{(rad)}\left(\Omega_a^2 n/2|\Delta_a|^2\right) \ll \gamma_D^{(rad)}$. In this case, the total radiated energy is finite and equal $\Omega_a^2 n/|\Delta_a|^2$. Thus, in the limit $\Omega_a \sim 1/\sqrt{V} \to 0$, $n_0 \sim V \to \infty$, and $\Omega_a\sqrt{n_0} \to$ const, the result is close to experiment—the spectrum is centered on the frequency of the selected mode ω_a and has a narrow line $\gamma_D^{(rad)}\left(\Omega_a^2 n/2|\Delta_a|^2\right) \ll \gamma_D^{(rad)}$.

However, the results of the described approach differ from experimental results and the results of the problem formulated with the classical field. In experiment, with time increase, the population of the excited state of an atom reaches the stationary state so that at each moment of time, some energy is radiated and some is absorbed from the external field. Then, in the dependence of the population inversion on time disappears (or time can be set approaching infinity, and the population remains finite). In Placzek's result, the population of the excited state, given by Eq. (6.2.6), exponentially depends on time, $\propto \exp\left(-\gamma_D^{(rad)}\left(\Omega_a^2 n/|\Delta_a|^2\right)t\right)$, and it tends to zero when time increases. This signifies that the system transitions from the state with n_0 photons to the state with $n_0 - 1$ photons, involving the emission of a single photon, and then the process stops. To ensure the correct behavior, as previously mentioned, one has to account for subsequent processes involving transitions between eigenstates and photon radiation. This is done below.

Consider the same limit as in the previous case, $\Omega_a \sim 1/\sqrt{V} \to 0$, $n_0 \sim V \to \infty$, and $\Omega_a\sqrt{n_0} \to \text{const}$. Above, we have taken into account only the transition between the states $|n_0, -\rangle$ and $|n_0 - 1, -\rangle$, and have solved equations for p_{n_0} and p_{n_0-1} from system (6.1.8). Now, we solve the full system.

If $n_0 \gg 1$, the rates of transitions between states for which $|n - n_0| \ll n_0$ are approximately the same, $\gamma_n = \gamma_D^{(rad)}\left(\Omega_a^2 n/|\Delta_a|^2\right) \approx \gamma_D^{(rad)}\left(\Omega_a^2 n_0/|\Delta_a|^2\right) \equiv \gamma_{\text{eff}}$. System (6.1.8), in which all transition rates are the same, corresponds to the Markov-Poisson process. In this case the solution to this system is well-known [7]:

$$\begin{aligned} p_{n_0}(t) &= \exp(-\gamma_{\text{eff}} t), \\ p_{n_0-1}(t) &= (\gamma_{\text{eff}} t)/1! \exp(-\gamma_{\text{eff}} t), \\ p_{n_0-k}(t) &= (\gamma_{\text{eff}} t)^k/k! \exp(-\gamma_{\text{eff}} t). \end{aligned} \tag{6.2.8}$$

Using solution (6.2.8), we find the average population of the excited state of the atom:

$$\left\langle \widehat{\sigma}^{\dagger}(t)\widehat{\sigma}(t) \right\rangle \simeq \left(\gamma_{\text{eff}}/\gamma_D^{(rad)}\right) \exp(-\gamma_{\text{eff}} t) \sum_{k=1}^{n_0} \frac{(\gamma_{\text{eff}} t)^k}{k!} \to_{n_0 \to \infty} \gamma_{\text{eff}}/\gamma_D^{(rad)} = \Omega_a^2 n_0/|\Delta_a|^2. \tag{6.2.9}$$

One can see that in the limit of a large initial number of photons in the selected mode, the population of the upper state of the atom reaches the constant value of $\gamma_{\text{eff}}/\gamma_D^{(rad)}$. This value is proportional to the square of the dipole moment $\Omega_a^2 \sim \omega_a d_{eg}^2/\hbar V$, which is obtained in the problem with the classical field.

For the two-time correlation function, using (6.1.10) we obtain:

$$\left\langle \widehat{\sigma}^{\dagger}(t+\tau)\widehat{\sigma}(t)\right\rangle \simeq \exp((i\omega_a-\gamma_{\text{eff}})\tau)\Omega_a^2 n_0/|\Delta_a|^2\exp(-\gamma_{\text{eff}}t)\sum_{k=1}^{n_0}\frac{(\gamma_{\text{eff}}t)^k}{k!}. \tag{6.2.10}$$

At times $t \ll n_0/\gamma_{\text{eff}}$, $\sum\limits_{k=n_0}^{1}\frac{(\gamma_{\text{eff}}t)^k}{k!}\sim \exp\left(\gamma_{eff}t\right)$, and we obtain:

$$\left\langle \widehat{\sigma}^{\dagger}(t_{\text{st}}+\tau)\widehat{\sigma}(t_{\text{st}})\right\rangle \simeq \Omega_a^2 n_0/|\Delta_a|^2\exp((i\omega_a-\gamma_{\text{eff}})\tau). \tag{6.2.11}$$

The condition $t \ll n_0/\gamma_{\text{eff}}$ reflects that during the system evolution, the number of photons in the selected mode does not significantly deviate from the initial value n_0.

The two-time correlation function corresponds to the spectrum centered on the frequency of the selected mode and has the width $\gamma_{\text{eff}} \ll \gamma_D^{(rad)}$. We also note that the two-time correlation function is calculated for the time greater than t_{st} for which the population of the excited state reaches the stationary value $\left(\Omega_a^2 n_0/\Delta_a^2\right)$. This corresponds to the spectrum measured in a system that has reached dynamic equilibrium.

For the radiation spectrum, we obtain:

$$\begin{aligned}
&\left\langle \widehat{a}_k^{\dagger}(t)\widehat{a}_k(t)\right\rangle \equiv n_k(t)\\
&\quad=\left|\sqrt{\frac{2\pi\omega_{a,k}}{V\hbar}}e_k\cdot d_{eg}\right|^2\int_0^t d\tau_2\int_0^t d\tau_1\left\langle \widehat{\sigma}^{\dagger}(\tau_2)\widehat{\sigma}(\tau_1)\right\rangle\exp(-i\omega_{a,k}(\tau_2-\tau_1))\\
&\quad\simeq\left|\sqrt{\frac{2\pi\omega_{a,k}}{V\hbar}}e_k\cdot d_{eg}\right|^2 t_{\text{st}}\pi\int_0^{\infty}d\tau\left\langle \widehat{\sigma}^{\dagger}(t_{\text{st}}+\tau)\widehat{\sigma}(t_{\text{st}})\right\rangle\exp(-i\omega_{a,k}\tau)\\
&\quad\simeq\left|\sqrt{\frac{2\pi\omega_{a,k}}{V\hbar}}e_k\cdot d_{eg}\right|^2\frac{t_{\text{st}}(\gamma_{\text{eff}})^2}{(\omega_{a,k}-\omega_a)^2+\left(\gamma_D^{(rad)}\Omega_a^2 n_0/\Delta_a^2\right)^2}.
\end{aligned} \tag{6.2.12}$$

We find the Lorentzian distribution of photons with frequencies centered on the frequency of the selected mode and having a narrow width $\gamma_{\text{eff}} \ll \gamma_D^{(rad)}$. The number of photons increases with time. This reflects that the system has reached dynamic equilibrium and emits photons continuously.

Let us compare the dynamics of the process obtained here with the dynamics in Placzek's theory. In the latter, it is assumed that the system transitions from the initial state to a given final state, but subsequent transitions are not considered. In the approach developed here, the system makes a cascade of transitions between the entangled states $|-,n\rangle$, until the system reaches its ground state $|g,0\rangle$.

Thus, we show that when all possible transitions between the eigenstates are taken into account, the population inversion of the atom reaches a quasistationary value that does not change until a large number of photons remain in the selected mode.

6.2.3 Coherent State of the Jaynes-Cummings Modes: Coherent Rayleigh Scattering

Experiments with incident laser light can be adequately described if the incident light is considered classical [8]. Such a description implies nonzero electric field amplitude and induced dipole moment.

Below, we assume that the incident field is quantized. Up to now, we assumed that the incident quantized light is in the Fock state, for which the expectation value of the electric field operator $\widehat{E} = \sqrt{4\pi\hbar\omega_a/V}\left(\widehat{a} + \widehat{a}^{\dagger}\right)$ is equal to zero:

$$\left\langle \widehat{E} \right\rangle = \sqrt{4\pi\hbar\omega_a/V}\left(\langle n_0|\widehat{a}|n_0\rangle + \langle n_0|\widehat{a}^{\dagger}|n_0\rangle\right) = 0 \tag{6.2.13}$$

As a result, the mean value of the dipole moment is also zero:

$$\begin{aligned}\langle\widehat{\sigma}(t)\rangle = {} & \cos\varphi_1\rho_{(g,0)(+,1)} - \sin\varphi_1\rho_{(g,0)(-,1)} \\ & + \sum_{n=2}^{\infty}(\cos\varphi_n \sin\varphi_{n-1}\rho_{(+,n-1)(+,n)} - \sin\varphi_n \sin\varphi_{n-1}\rho_{(+,n-1)(-,n)} \\ & + \cos\varphi_n \cos\varphi_{n-1}\rho_{(-,n-1)(+,n)} - \sin\varphi_n \cos\varphi_{n-1}\rho_{(-,n-1)(-,n)}) = 0.\end{aligned} \tag{6.2.14}$$

When we consider the field as classical, we assume that the field is coherent and the amplitude of the electric field is nonzero, $E \neq 0$. Consequently, the induced dipole moment has nonzero amplitude, $\langle\widehat{\sigma}\rangle \neq 0$ (see Eq. (3.4.32)).

To resolve the discrepancy between Eq. (6.2.13) and the requirement $E \neq 0$, we should design such quantum states of the incident light that are most similar to the classic light and reproduce the results on Rayleigh scattering of classical light considered in Chaps. 3 and 4. These quantum states are the coherent states discussed in Chap. 5. We should consider the coherent quantum state of the field as the initial condition, i.e., instead of $\widehat{\rho}(0) = |g, n_0\rangle\langle g, n_0|$, take $\widehat{\rho}(0) = |g, \alpha\rangle\langle g, \alpha|$, where

$$|\alpha\rangle = \exp\left(-|\alpha|^2/2\right)\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}|n\rangle$$

is the coherent state of the field.

Now, we find the system dynamics by solving Eq. (6.1.4) for the system density matrix in the limit of a large frequency detuning, $\Omega_a^2|\alpha|^2/\Delta^2 \ll 1$, a large amplitude of the exciting field, $|\alpha|^2 \gg 1$ (supposing that α is real), and on the time scale $t \gg 1/\gamma_D^{(rad)}$. Having the density matrix, we can calculate the expectation values of any operator. The result for the expectation value of the atomic dipole moment is (see Problem 1.25)

$$\langle\widehat{\sigma}(t)\rangle \simeq -\frac{e^{-i\omega_{ext}t}\Omega_R\alpha}{\Delta_a}\exp\left(-\frac{|\alpha|^2\gamma_D^{(rad)}\Omega_R^2}{|\Delta_a|^2}t\right). \tag{6.2.15}$$

From Eq. (6.2.15) it follows that the expectation value of the atomic dipole moment, $\langle\widehat{\sigma}(t)\rangle$, decays in time with the rate $|\alpha|^2\gamma_D^{(rad)}\Omega_R^2/|\Delta_a|^2$. The physical reason for this is that the energy from the incident field is radiated into the free space and, consequently, dissipates. As a result, the amplitude of the incident field decreases, and the atomic dipole moment also decreases. However, if we suppose that during the time interval $\left(\gamma_D^{(rad)}\right)^{-1} \ll t \ll \left(|\alpha|^2\gamma_D^{(rad)}\Omega_a^2/|\Delta_a|^2\right)^{-1}$ we have $\exp\left(-\left(|\alpha|^2\gamma_D^{(rad)}\Omega_R^2/|\Delta_a|^2\right)t\right) \sim 1$, i.e., the decrease of the $|\langle\widehat{\sigma}(t)\rangle|$ value is negligible (see Eq. (6.2.15)), we obtain:

$$|\langle\widehat{\sigma}(t)\rangle| \simeq \frac{\Omega_a\alpha}{\Delta_a}. \tag{6.2.16}$$

Let us compare this result with the one obtained for the classical field, which amplitude does not change with time (see Eq. (3.4.33)). When the difference between the frequency of the external field and the TLS transition frequency, $\omega_{ext} - \omega_\sigma$, is much larger than the dissipation rate γ_σ, Eq. (3.4.33) simplifies to Eq. (6.2.16):

$$\langle\widehat{\sigma}\rangle \simeq -\frac{\Omega_{ext}(\omega_{ext}-\omega_\sigma)}{(\omega_{ext}-\omega_\sigma)^2}e^{-i\omega_{ext}t} = -\frac{\Omega_{ext}}{\Delta_a}e^{-i\omega_{ext}t} \tag{6.2.17}$$

Note that $\Omega_a\alpha = -d_{eg}\sqrt{4\pi\omega_a/\hbar V}\alpha = -d_{eg}\langle E\rangle/\hbar$ and, therefore, corresponds to the classical value $\Omega_{ext} = -d_{eg}E/\hbar$. Thus, Eq. (6.2.16) reproduces the result obtained for the classical field. The spectrum of oscillations given by Eq. (6.2.16), $S(\omega) = (2\pi(\Omega_a\alpha)^2/|\Delta_a|^2)\delta(\omega - \omega_{ext})$, reproduces the spectrum of Rayleigh scattering of classical field (the red vertical line in Fig. 5.4).

To conclude, in Chap. 6, we have shown that an incidence of the quantized field gives a result different from the Rayleigh scattering described classically. Namely, due to quantum fluctuations, scattered light has a finite linewidth. Although the linewidth of the scattered field is finite, it is nevertheless much narrower than the spontaneous emission line.

The inelastic scattering of a quantized field is caused by the fact that in order to radiate, a quantum system must interact with a reservoir of free space modes. It is this interaction that can change the frequency of emitted photons. In classical physics, the influence of this interaction on the external field is neglected, and the scattering is elastic. This influence is especially strong in the single-photon scattering, in which it leads to the disappearance of the incident field. If the number of incident photons is finite, even if only one photon is scattered, we have a finite linewidth. Moreover, when an incident wave is coherent, a finite linewidth arises due to a decrease in the total number of photons in the incident state.

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Chapter 7
Summary of Part I

Often, photon scattering is considered as a particular case of the spectroscopic theory of absorption and emission of photons during the transition of an atom between its states. This theory assumes that the transitions are caused by the incident field. In the first order of the perturbation theory, according to Fermi's golden rule, the probability of the transition between initial and final states, which is caused by the dipole interaction $\widehat{V} = -\mathbf{d} \cdot \mathbf{E}$, is proportional to $\left|\langle i|\widehat{V}|f\rangle\right|^2$ [1]. For elastic scattering, the matrix elements of the dipole moment between the same atomic states are zero, $\left|\langle i|\widehat{V}|f\rangle\right|^2 = 0$; therefore, one usually employs the second order of the perturbation theory. The resulting formula interprets the elastic scattering of light as a two-step process. In the first step, the atom in the ground state absorbs an incident photon and transitions to an excited state, which is a superposition of excited atomic states. In the second step, the excited atom emits a photon.

In Part I, we have shown that such an often-used scheme, in which transitions between states of a quantum system are caused by an external resonant field, is not applicable to Hermitian systems. Indeed, if an atom and a single mode of incident light comprise a closed interacting Hermitian system (a dressed atom), we observe the endlessly repeating energy exchange between the atom and the mode [2, 3]. To study such an exchange, we cannot restrict ourselves to the first or second orders of the perturbation theory but should consider the whole series.

Our approach is based on the fact that continuous energy exchange within the dressed atom does not require an exact match of the energy difference between eigenstates and the photon energy. Radiation or light scattering by the atom occurs; it introduces a new participant—a photon in the mode distinct from the incident one. Moreover, in this part, the irreversible radiation of a photon requires a continuum of additional modes.

To conclude, we consider the illuminated system (atom or molecule) and scattered (incident) mode of light as an open quantum system interacting with the reservoir of free space modes. The problem of light scattering becomes much more

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complex than the problems solved in Bohr's scheme. To avoid dealing with an infinite number of reservoir states, in Part I, we search for the solution to the scattering problem in two steps. First, following well-known algorithms [4, 5], we describe the interaction with the reservoir by introducing dissipative and noise terms. As a result, the dynamics of the dressed atom has to be described by the Lindblad equation or the Heisenberg-Langevin operator equations. In physical terms, this implies that scattering is achieved through interaction with a reservoir of free space modes.

As demonstrated in Sects. 12.2 and 12.3, the scattering spectrum is interpreted as a perturbation of the reservoir of free space modes. The associated damping constants and noise amplitudes are found while excluding the reservoir variables from the equations for a closed system comprised of the dressed atom and the reservoir of free space modes.

Subsequently, we solve the resulting equations, but the solution only describes the evolution of the dressed atom. Because we utilize the Born approximation to exclude the reservoir variables, the radiation spectrum cannot be found at this step.

To find the spectrum, we solve the problem of photon emission by the dressed atom. We imply that the perturbation of the reservoir modes is induced by the dipole moment of the dressed atom, which is found in the previous step. In our case, this is the reservoir of free space modes that do not include the incident field.

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Chapter 8
Problems for Part I

Problem 1.1
Show that in the Schrödinger picture, a TLS interacting with a single mode of a monochromatic external field is in the regime of Rabi oscillations.

Solution
The unperturbed TLS is described by the time-independent Hamiltonian H_0 with only two orthogonal eigenstates:

$$H_0|e\rangle = E_e|e\rangle, \qquad H_0|g\rangle = E_g|g\rangle \tag{8.1.1}$$

which correspond to the excited state with the wave function $|e\rangle$ having the energy $E_e = \hbar\omega_e$ and the ground state with the wave function $|g\rangle$, whose energy is $E_g = \hbar\omega_g$. These wave functions evolve with the exponential factors $\exp(-i\omega_{e,\ g}t)$. Indeed,

$$i\hbar\frac{\partial}{\partial t}\exp(-i\omega_e t)|e\rangle = \hbar\omega_e \exp(-i\omega_e t)|e\rangle = \exp(-i\omega_e t)\hat{H}_0|e\rangle = E_e \exp(-i\omega_e t)|e\rangle$$

Since $|g\rangle$ and $|e\rangle$ constitute a complete set, any TLS state can be expressed as a linear combination of these functions:

$$|\Psi(t)\rangle = c_e \exp(-i\omega_e t)|e\rangle + c_g \exp\big(-i\omega_g t\big)|g\rangle \tag{8.1.2}$$

Now, we obtain the Hamiltonian $\hat{V}$ of the dipole interaction of the TLS with an external monochromatic field $\mathbf{E}(t) = \mathbf{E}_{ext}(\exp(-i\omega_{ext}t) + \exp(i\omega_{ext}t))/2$. We recall that diagonal matrix elements of the operator of the dipole moment are zero, $\langle g|\hat{d}|g\rangle = d_{gg} = 0$ and $\langle e|\hat{d}|e\rangle = 0$. Assuming the TLS to be spherically symmetric and using the rotated wave approximation, we can write:

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$$\hat{V} = -\mathbf{d}\cdot\mathbf{E} \approx -\frac{1}{2}d_{eg}E_{ext}\left(\exp(-i\omega_{ext}t)\hat{\sigma} + \exp(i\omega_{ext}t)\hat{\sigma}^{\dagger}\right), \tag{8.1.3}$$

The wave function $|\Psi(t)\rangle$ of the Hamiltonian $\hat{H}_0 + \hat{V}$ can still be searched in the form:

$$|\Psi(t)\rangle = c_e(t)\exp(-i\omega_e t)|e\rangle + c_g(t)\exp\left(-i\omega_g t\right)|g\rangle, \tag{8.1.4}$$

where the coefficients $c_e(t)$ and $c_g(t)$ are unknown time-dependent functions. Wave function (8.1.4) satisfies the Schrödinger equation with time-dependent Hamiltonian:

$$i\hbar\frac{\partial}{\partial t}\Psi(t) = \left[\hat{H}_0 + \hat{V}(t)\right]\Psi(t) \tag{8.1.5}$$

Substituting Eq. (8.1.4) into Eq. (8.1.5), we obtain:

$$\begin{aligned} &i\hbar\left[\exp(-i\omega_e t)\frac{\partial}{\partial t}c_e(t)\right]|e\rangle + i\hbar\left[\exp\left(-i\omega_g t\right)\frac{\partial}{\partial t}c_g(t)\right]|g\rangle \\ &\quad + \left[c_e(t)\exp(-i\omega_e t)(\hbar\omega_e)|e\rangle + c_g(t)\exp\left(-i\omega_g t\right)\left(\hbar\omega_g\right)\right]|g\rangle \\ &= \left[c_e(t)\exp(-i\omega_e t)H_0|e\rangle + c_g(t)\exp\left(-i\omega_g t\right)H_0|g\rangle\right. \\ &\quad \left. + \hat{V}(t)c_e(t)\exp(-i\omega_e t)|e\rangle + \hat{V}(t)c_g(t)\exp\left(-i\omega_g t\right)|g\rangle\right] \end{aligned} \tag{8.1.6}$$

Noting that the last two terms on the left-hand side cancel the first two terms on the right-hand side, we arrive at

$$\begin{aligned} &i\hbar\exp(-i\omega_e t)\frac{\partial}{\partial t}c_e(t)|e\rangle + i\hbar\exp\left(-i\omega_g t\right)\frac{\partial}{\partial t}c_g(t)|g\rangle \\ &= \left[\hat{V}c_e(t)\exp(-i\omega_e t)|e\rangle + \hat{V}c_g(t)\exp\left(-i\omega_g t\right)|g\rangle\right] \end{aligned} \tag{8.1.7}$$

To find the equations for $\frac{\partial}{\partial t}c_e(t)$ and $\frac{\partial}{\partial t}c_g(t)$, we take the inner products of Eq. (8.1.7) separately by $\langle e|$ and $\langle g|$. Due to the orthogonality of the eigenfunctions, we obtain two differential equations:

$$\frac{\partial}{\partial t}c_e(t) = -\frac{i}{\hbar}\left[c_e(t)\langle e|\hat{V}|e\rangle + c_g(t)\langle e|\hat{V}|g\rangle\exp(i\omega_\sigma t)\right] \tag{8.1.8}$$

and

$$\frac{\partial}{\partial t}c_g(t) = -\frac{i}{\hbar}\left[c_g(t)\langle g|\hat{V}|g\rangle + c_e(t)\langle g|\hat{V}|e\rangle\exp(-i\omega_\sigma t)\right] \tag{8.1.9}$$

According to properties of the operators $\hat{\sigma}$ and $\hat{\sigma}^\dagger$, we have:

$$\langle e|\hat{\sigma}|e\rangle = \langle e|\hat{\sigma}^\dagger|e\rangle = \langle g|\hat{\sigma}|g\rangle = \langle g|\hat{\sigma}^\dagger|g\rangle = 0,$$
$$\langle g|\hat{\sigma}|e\rangle = \langle e|\hat{\sigma}^\dagger|g\rangle = 1, \quad \langle e|\hat{\sigma}|g\rangle = \langle g|\hat{\sigma}^\dagger|e\rangle = 0.$$

Using Eq. (8.1.3) and notation, $\Omega = -d_{eg}E_{ext}/(2\hbar)$ and $\Delta_\omega = \omega_{ext} - \omega_\sigma$, we rewrite Eqs. (8.1.8) and (8.1.9) as

$$\frac{\partial}{\partial t}c_e = -i\Omega_{ext}e^{-i\Delta_\omega t}c_g, \tag{8.1.10}$$

$$\frac{\partial}{\partial t}c_g = -i\Omega_{ext}e^{+i\Delta_\omega t}c_e, \tag{8.1.11}$$

These equations still have time-dependent coefficients. Using new variables $B_g = c_g e^{-i\Delta_\omega t/2}$ and $B_e = c_e e^{i\Delta_\omega t/2}$, we arrive at the equations which can be written in the matrix form with the coefficient matrix independent on time:

$$\frac{\partial}{\partial t}\begin{bmatrix} B_e(t) \\ B_g(t) \end{bmatrix} = \begin{bmatrix} +\dfrac{i\Delta_\omega}{2} & i\Omega_{ext} \\ i\Omega_{ext} & -\dfrac{i\Delta_\omega}{2} \end{bmatrix}\begin{bmatrix} B_e(t) \\ B_g(t) \end{bmatrix} \tag{8.1.12}$$

Time independence of the coefficient matrix allows us to search for the solution to Eq. (8.1.12) in the form:

$$\begin{bmatrix} B_e(t) \\ B_g(t) \end{bmatrix} = \exp(\lambda t)\begin{bmatrix} B_e \\ B_g \end{bmatrix},$$

where λ is the root of the equation

$$\begin{vmatrix} \dfrac{i\Delta_\omega}{2} - \lambda & i\Omega_{ext} \\ i\Omega_{ext} & -\dfrac{i\Delta_\omega}{2} - \lambda \end{vmatrix} = 0 \tag{8.1.13}$$

The solutions to this equation are $\lambda = \pm i\Omega_\Delta$, where $\Omega_\Delta^2 = \Omega_{ext}^2 + \Delta_\omega^2/4$ is the Rabi frequency and corresponding eigenvectors are

$$\mathbf{B}_+ = \begin{bmatrix} 1 \\ (\Omega_\Delta - \Delta_\omega/2)/\Omega_{ext} \end{bmatrix} \text{ and } \mathbf{B}_- = \begin{bmatrix} -1 \\ (\Omega_\Delta + \Delta_\omega/2)/\Omega_{ext} \end{bmatrix}$$

The solution to Eq. (8.1.12) is a linear combination of the eigenvectors:

$$\begin{bmatrix} B_e \\ B_g \end{bmatrix} = C_1 \begin{bmatrix} 1 \\ (\Omega_\Delta - \Delta_\omega/2)/\Omega_{ext} \end{bmatrix} e^{+i\Omega_\Delta t} + C_2 \begin{bmatrix} -1 \\ (\Omega_\Delta + \Delta_\omega/2)/\Omega_{ext} \end{bmatrix} e^{-i\Omega_\Delta t}. \tag{8.1.14}$$

In particular, assuming that initially, the TLS is unexcited ($c_e(0) = 0$ and $c_g(0) = 1$), we observe the Rabi cycle:

$$c_e(t) = \frac{i\Omega_{ext}}{\Omega_\Delta} \sin(\Omega_\Delta t) e^{-\frac{i\Delta_\omega t}{2}}, c_g(t) = \left[\cos(\Omega_\Delta t) - \frac{i\Delta_\omega/2}{\Omega_\Delta} \sin(\Omega_\Delta t)\right] e^{\frac{i\Delta_\omega t}{2}}.$$

One can verify that the sum of the probabilities of finding the TLS in either excited or ground states is $\left|c_g^2(t)\right| + \left|c_e^2(t)\right| = 1$. The physical meaning of the expression for the Rabi oscillations becomes clear. Under the action of a light wave, an initially unexcited TLS transitions into an excited state with the probability:

$$p(t) = c_e(t)c_e^*(t) = \left(\frac{\Omega_{ext}}{\Omega_\Delta}\right)^2 \sin^2(\Omega_\Delta t) = \frac{1}{2}\left(\frac{\Omega_{ext}}{\Omega_\Delta}\right)^2 (1 - \cos(2\Omega_\Delta t))$$

that oscillates with the Rabi frequency $2\Omega_\Delta$. The maximum amplitude of these oscillations is equal to unity and is achieved in the resonant case $\Delta = 0$. That is in agreement with Eq. (2.4.19)—the result obtained in the Heisenberg picture.

Problem 1.2

Derive the Heisenberg equations for operators $\hat{\sigma}$, $\hat{\sigma}^\dagger$, and $\hat{\sigma}^\dagger\hat{\sigma}$ in the Heisenberg picture employing the Rabi Hamiltonian:

$$\hat{H} = \hbar\omega_\sigma \hat{\sigma}^\dagger\hat{\sigma} + \hbar\Omega_{ext}\left(\hat{\sigma} + \hat{\sigma}^\dagger\right)\left(e^{-i\omega_{ext}t} + e^{i\omega_{ext}t}\right) \tag{8.2.1}$$

Solution

The Heisenberg equation for an arbitrary operator $\hat{A}$ is

$$d\hat{A}/dt = (i/\hbar)\left[\hat{H}, \hat{A}\right] \tag{8.2.2}$$

Using Eq. (8.2.2) with Hamiltonian (8.2.1), we obtain:

$$\frac{d}{dt}\hat{\sigma}_H = i\left(\omega_\sigma\left[\hat{\sigma}_H^\dagger\hat{\sigma}_H, \hat{\sigma}_H\right] + \Omega_{ext}\left(e^{i\omega_{ext}t} + e^{-i\omega_{ext}t}\right)\left(\left[\hat{\sigma}_H, \hat{\sigma}_H\right] + \left[\hat{\sigma}_H^\dagger, \hat{\sigma}_H\right]\right)\right) \tag{8.2.3}$$

$$\frac{d}{dt}\hat{\sigma}_H^\dagger = i\left(\omega_\sigma\left[\hat{\sigma}_H^\dagger\hat{\sigma}_H, \hat{\sigma}^\dagger\right] + \Omega_{ext}\left(e^{i\omega_{ext}t} + e^{-i\omega_{ext}t}\right)\left(\left[\hat{\sigma}_H, \hat{\sigma}_H^\dagger\right] + \left[\hat{\sigma}_H^\dagger, \hat{\sigma}_H^\dagger\right]\right)\right) \tag{8.2.4}$$

$$\frac{d}{dt}\hat{\sigma}_H^\dagger\hat{\sigma}_H = i\Big(\omega_\sigma\Big[\hat{\sigma}_H^\dagger\hat{\sigma}_H, \hat{\sigma}_H^\dagger\hat{\sigma}_H\Big] + \Omega_{ext}\big(e^{i\omega_{ext}t} + e^{-i\omega_{ext}t}\big)\Big(\Big[\hat{\sigma}_H^\dagger, \hat{\sigma}_H^\dagger\hat{\sigma}_H\Big] + \Big[\hat{\sigma}_H, \hat{\sigma}_H^\dagger\hat{\sigma}_H\Big]\Big)\Big) \tag{8.2.5}$$

The commutation relations included in these equations can be calculated using the definitions:

$$\hat{\sigma} = |g\rangle\langle e|, \hat{\sigma}^\dagger = |e\rangle\langle g|,$$

Taking $\langle e|g\rangle = \langle g|e\rangle = 0, \quad \langle e|e\rangle = \langle g|g\rangle = 1$ into account, we obtain:

$$\begin{aligned}
&\hat{\sigma}\hat{\sigma} = |g\rangle\langle e|g\rangle\langle e| = 0,\\
&\hat{\sigma}^\dagger\hat{\sigma}^\dagger = |e\rangle\langle g|e\rangle\langle g| = 0,\\
&\hat{\sigma}\hat{\sigma}^\dagger\hat{\sigma} = |g\rangle\langle e|e\rangle\langle g|g\rangle\langle e| = |g\rangle\langle e| = \hat{\sigma},\\
&\hat{\sigma}^\dagger\hat{\sigma}\hat{\sigma}^\dagger = |e\rangle\langle g|g\rangle\langle e|e\rangle\langle g| = |g\rangle\langle e| = \hat{\sigma}^\dagger,\\
&\hat{\sigma}^\dagger\hat{\sigma} + \hat{\sigma}\hat{\sigma}^\dagger = |e\rangle\langle e| + |g\rangle\langle g| = \hat{I},\\
&\hat{\sigma}^\dagger\hat{\sigma} - \hat{\sigma}\hat{\sigma}^\dagger = |e\rangle\langle e| - |g\rangle\langle g| = \hat{D},\\
&\hat{\sigma}^\dagger\hat{\sigma} = \frac{1}{2}\big(\hat{I} + \hat{D}\big), \quad \hat{\sigma}\hat{\sigma}^\dagger = \frac{1}{2}\big(\hat{I} - \hat{D}\big),
\end{aligned}$$

where $\hat{D}$ is the population inversion operator. The expressions for the required commutation relations are

$$\big[\hat{\sigma}^\dagger\hat{\sigma}, \hat{\sigma}\big] = \hat{\sigma}^\dagger\hat{\sigma}\hat{\sigma} - \hat{\sigma}\hat{\sigma}^\dagger\hat{\sigma} = -\hat{\sigma}. \tag{8.2.6}$$

$$\big[\hat{\sigma}^\dagger\hat{\sigma}, \hat{\sigma}^\dagger\big] = \hat{\sigma}^\dagger\hat{\sigma}\hat{\sigma}^\dagger - \hat{\sigma}^\dagger\hat{\sigma}^\dagger\hat{\sigma} = \hat{\sigma}^\dagger \tag{8.2.7}$$

$$\big[\hat{\sigma}^\dagger\hat{\sigma}, \hat{\sigma}^\dagger\hat{\sigma}\big] = 0 \tag{8.2.8}$$

$$\big[\hat{\sigma}, \hat{\sigma}^\dagger\big] = \hat{\sigma}\hat{\sigma}^\dagger - \hat{\sigma}^\dagger\hat{\sigma} = \hat{I} - 2\hat{\sigma}^\dagger\hat{\sigma} = -\hat{D}. \tag{8.2.9}$$

Substituting Eqs. (8.2.6)–(8.2.9) into Eqs. (8.2.3)–(8.2.5), we obtain the required equations:

$$\begin{aligned}
\frac{d\hat{\sigma}}{dt} &= i\big[\hat{H}, \hat{\sigma}\big] = -i\omega_\sigma\hat{\sigma} + i\Omega_{ext}\big(e^{i\omega_{ext}t} + e^{-i\omega_{ext}t}\big)\big(2\hat{\sigma}^\dagger\hat{\sigma} - \hat{I}\big),\\
\frac{d\hat{\sigma}^\dagger}{dt} &= i\big[\hat{H}, \hat{\sigma}^\dagger\big] = i\omega_\sigma\hat{\sigma}^\dagger - i\Omega_{ext}\big(e^{i\omega_{ext}t} + e^{-i\omega_{ext}t}\big)\big(2\hat{\sigma}^\dagger\hat{\sigma} - \hat{I}\big),\\
\frac{d\hat{\sigma}^\dagger\hat{\sigma}}{dt} &= i\big[\hat{H}, \hat{\sigma}^\dagger\hat{\sigma}\big] = i\Omega_{ext}\big(e^{i\omega_{ext}t} + e^{-i\omega_{ext}t}\big)\big(\hat{\sigma} - \hat{\sigma}^\dagger\big).
\end{aligned} \tag{8.2.10}$$

Formally, Eq. (8.2.10) can be rewritten as linear equations by using the operator $\hat{D}$:

$$\frac{d\hat{\sigma}}{dt} = -i\omega_\sigma\hat{\sigma} + i\Omega_{ext}\hat{D}e^{-i\omega_{ext}t} + i\Omega_{ext}\hat{D}e^{i\omega_{ext}t}$$

$$\frac{d\hat{\sigma}^\dagger}{dt} = i\omega_\sigma\hat{\sigma}^\dagger - i\Omega\hat{D}e^{i\omega_{ext}t} - i\Omega\hat{D}e^{i\omega_{ext}t}$$

$$\frac{d\hat{D}}{dt} = 2i\Omega\left(\hat{\sigma}e^{i\omega_{ext}t} - \hat{\sigma}^\dagger e^{-i\omega_{ext}t}\right) + 2i\Omega\left(\hat{\sigma}e^{-i\omega_{ext}t} - \hat{\sigma}^\dagger e^{i\omega_{ext}t}\right)$$

After introducing auxiliary variables $\widehat{\widetilde{\sigma}}_H(t) = \hat{\sigma}_H \exp(i\omega_{ext}t)$ and $\widehat{\widetilde{\sigma}}_H^\dagger(t) = \hat{\sigma}_H^\dagger(t)$ $\exp(-i\omega_{ext}t)$, these equations are equivalent to Eqs. (2.4.6)–(2.4.8).

Problem 1.3
Prove that the solution to the system of equations (Eqs. (2.4.9)–(2.4.11) from the main text)

$$\frac{d\widehat{\widetilde{\sigma}}}{dt} = i\Delta_\omega\widehat{\widetilde{\sigma}} + i\Omega_{ext}\hat{D} \tag{8.3.1}$$

$$\frac{d\widehat{\widetilde{\sigma}}^\dagger}{dt} = -i\Delta_\omega\widehat{\widetilde{\sigma}}^\dagger - i\Omega_{ext}\hat{D} \tag{8.3.2}$$

$$\frac{d\hat{D}}{dt} = 2i\Omega_{ext}\left(\widehat{\widetilde{\sigma}} - \widehat{\widetilde{\sigma}}^\dagger\right) \tag{8.3.3}$$

is

$$\begin{aligned}\hat{\sigma}(t) = {} & \left[\Omega_{ext}^2/2\Omega_\Delta^2 + \left(1 - \Omega_{ext}^2/2\Omega_\Delta^2\right)\cos(2\Omega_\Delta t) + (i\Delta_\omega/2\Omega_\Delta)\sin(2\Omega_\Delta t)\right]\hat{\sigma}(0) \\ & + \left(\Omega_{ext}^2/2\Omega_\Delta^2\right)(1 - \cos(2\Omega_\Delta t))\hat{\sigma}^\dagger(0) \\ & + \left[\left(\Delta_\omega\Omega_{ext}/4\Omega_\Delta^2\right)(\cos(2\Omega_\Delta t) - 1) + (i\Omega_{ext}/2\Omega_\Delta)\sin(2\Omega_\Delta t)\right]\hat{D}(0)\end{aligned} \tag{8.3.4}$$

$$\begin{aligned}\hat{\sigma}^\dagger(t) = {} & \left(\Omega_{ext}^2/2\Omega_\Delta^2\right)(1 - \cos(2\Omega_\Delta t))\hat{\sigma}(0) \\ & + \left[\Omega_{ext}^2/2\Omega_\Delta^2 + \left(1 - \Omega_{ext}^2/2\Omega_\Delta^2\right)\cos(2\Omega_\Delta t) - (i\Delta_\omega/2\Omega_\Delta)\sin(2\Omega_\Delta t)\right]\hat{\sigma}^\dagger(0) \\ & + \left[\left(\Delta_\omega\Omega_{ext}/4\Omega_\Delta^2\right)(\cos(2\Omega_\Delta t) - 1) - (i\Omega_{ext}/2\Omega_\Delta)\sin(2\Omega_\Delta t)\right]\hat{D}(0)\end{aligned} \tag{8.3.5}$$

$$\begin{aligned}\hat{D}(t) = {} & \left[\left(\Delta_\omega\Omega_{ext}/2\Omega_\Delta^2\right)(\cos(2\Omega_\Delta t) - 1) + (i\Omega_{ext}/\Omega_\Delta)\sin(2\Omega_\Delta t)\right]\hat{\sigma}(0) \\ & + \left[\left(\Delta_\omega\Omega_{ext}/2\Omega_\Delta^2\right)(\cos(2\Omega_\Delta t) - 1) - (i\Omega_{ext}/\Omega_\Delta)\sin(2\Omega_\Delta t)\right]\hat{\sigma}^\dagger(0) \\ & + \left[\left(\Delta_\omega^2/4\Omega_\Delta^2\right) + \left(\Omega_{ext}^2/\Omega_\Delta^2\right)\cos(\Omega_\Delta t)\right]\hat{D}(0)\end{aligned} \tag{8.3.6}$$

Solution
Systems (8.3.1)–(8.3.3) can be written in the matrix form as follows:

$$\frac{d}{dt}\begin{pmatrix}\hat{\tilde{\sigma}}\\ \hat{\tilde{\sigma}}^{\dagger}\\ \hat{D}\end{pmatrix}=\begin{pmatrix}i\Delta_{\omega} & 0 & i\Omega_{ext}\\ 0 & -i\Delta_{\omega} & -i\Omega_{ext}\\ 2i\Omega_{ext} & -2i\Omega_{ext} & 0\end{pmatrix}\begin{pmatrix}\hat{\tilde{\sigma}}\\ \hat{\tilde{\sigma}}^{\dagger}\\ \hat{D}\end{pmatrix} \tag{8.3.7}$$

Since the coefficient matrix is time-independent, we can search for the solution to Eq. (8.3.7) in the form:

$$\mathbf{h}(t)=\begin{pmatrix}\hat{\tilde{\sigma}}(t)\\ \hat{\tilde{\sigma}}^{\dagger}(t)\\ \hat{D}(t)\end{pmatrix}=\exp(\lambda t)\mathbf{h},$$

reducing Eq. (8.3.7) to the eigenvalue problem $\mathbf{M}\cdot\mathbf{h}=\lambda\mathbf{h}$ for the matrix

$$\mathbf{M}=\begin{pmatrix}i\Delta_{\omega} & 0 & i\Omega_{ext}\\ 0 & -i\Delta_{\omega} & -i\Omega_{ext}\\ 2i\Omega_{ext} & -2i\Omega_{ext} & 0\end{pmatrix}.$$

The eigenvalues of the matrix $\mathbf{M}$ are $\lambda_1=0$ and $\lambda_{2,3}=\pm i\sqrt{\Delta_{\omega}^2+4\Omega_{ext}^2}$, and the corresponding eigenvectors are

$$\begin{aligned}\mathbf{h}_1&=\begin{pmatrix}-\Omega_{ext}/\Delta_{\omega}\\ -\Omega_{ext}/\Delta_{\omega}\\ 1\end{pmatrix},\mathbf{h}_{2,3}\\ &=\begin{pmatrix}\pm\sqrt{\Delta_{\omega}^2+4\Omega_{ext}^2}/2\Omega_{ext}\mp\Omega_{ext}/\left(\pm\Delta_{\omega}+\sqrt{\Delta_{\omega}^2+4\Omega_{ext}^2}\right)\\ \mp\Omega_{ext}/\left(\pm\Delta_{\omega}+\sqrt{\Delta_{\omega}^2+4\Omega_{ext}^2}\right)\\ 1\end{pmatrix}\end{aligned} \tag{8.3.8}$$

The general solution of system (8.3.7) is

$$\begin{pmatrix}\hat{\tilde{\sigma}}(t)\\ \hat{\tilde{\sigma}}^{\dagger}(t)\\ \hat{D}(t)\end{pmatrix}=\hat{c}_1\mathbf{h}_1e^{\lambda_1 t}+\hat{c}_2\mathbf{h}_2e^{\lambda_2 t}+\hat{c}_3\mathbf{h}_3e^{\lambda_3 t} \tag{8.3.9}$$

where the unknown time-independent operators $\hat{c}_{1,2,3}$ are determined by the initial values of operators $\hat{\tilde{\sigma}}$, $\hat{\tilde{\sigma}}^{\dagger}$, and $\hat{D}$

$$
\begin{pmatrix} \widehat{\tilde{\sigma}}(0) \\ \widehat{\tilde{\sigma}}^{\dagger}(0) \\ \hat{D}(0) \end{pmatrix} = \hat{c}_1\mathbf{h}_1 + \hat{c}_2\mathbf{h}_2 + \hat{c}_3\mathbf{h}_3
$$

$$
= \hat{c}_1 \begin{pmatrix} -\Omega_{ext}/\Delta_\omega \\ -\Omega_{ext}/\Delta_\omega \\ 1 \end{pmatrix} + \hat{c}_2 \begin{pmatrix} \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}/2\Omega_{ext} - \Omega_{ext}/\left(\Delta_\omega + \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}\right) \\ -\Omega_{ext}/\left(\Delta_\omega + \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}\right) \\ 1 \end{pmatrix}
$$

$$
+ \hat{c}_3 \begin{pmatrix} -\sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}/2\Omega_{ext} + \Omega_{ext}/\left(-\Delta_\omega + \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}\right) \\ \Omega_{ext}/\left(-\Delta_\omega + \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}\right) \\ 1 \end{pmatrix}
$$

$$
= \begin{pmatrix} -\Omega_{ext}/\Delta_\omega & \dfrac{\sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}}{2\Omega_{ext}} - \dfrac{\Omega_{ext}}{\Delta_\omega + \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}} & -\dfrac{\sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}}{2\Omega_{ext}} + \dfrac{\Omega_{ext}}{-\Delta_\omega + \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}} \\ -\Omega_{ext}/\Delta_\omega & -\dfrac{\Omega_{ext}}{\Delta_\omega + \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}} & \dfrac{\Omega_{ext}}{-\Delta_\omega + \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}} \\ 1 & 1 & 1 \end{pmatrix}
$$

$$
\times \begin{pmatrix} \hat{c}_1 \\ \hat{c}_2 \\ \hat{c}_3 \end{pmatrix} \tag{8.3.10}
$$

From system (8.3.10), we obtain:

$$
\begin{pmatrix} \hat{c}_1 \\ \hat{c}_2 \\ \hat{c}_3 \end{pmatrix} = \begin{pmatrix} -\dfrac{2\Delta_\omega\Omega_{ext}}{\Delta_\omega^2 + 4\Omega_{ext}^2} & -\dfrac{2\Delta_\omega\Omega_{ext}}{\Delta_\omega^2 + 4\Omega_{ext}^2} & \dfrac{\Delta_\omega^2}{\Delta_\omega^2 + 4\Omega_{ext}^2} \\ \dfrac{\Omega_{ext}\left(\Delta_\omega - \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}\right)}{\Delta_\omega^2 + 4\Omega_{ext}^2} & \dfrac{\Omega_{ext}\left(\Delta_\omega + \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}\right)}{\Delta_\omega^2 + 4\Omega_{ext}^2} & \dfrac{2\Omega_{ext}^2}{\Delta_\omega^2 + 4\Omega_{ext}^2} \\ \dfrac{\Omega_{ext}\left(\Delta_\omega + \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}\right)}{\Delta_\omega^2 + 4\Omega_{ext}^2} & \dfrac{\Omega_{ext}\left(\Delta_\omega - \sqrt{\Delta_\omega^2 + 4\Omega_{ext}^2}\right)}{\Delta_\omega^2 + 4\Omega_{ext}^2} & \dfrac{2\Omega_{ext}^2}{\Delta_\omega^2 + 4\Omega_{ext}^2} \end{pmatrix} \begin{pmatrix} \widehat{\tilde{\sigma}}(0) \\ \widehat{\tilde{\sigma}}^{\dagger}(0) \\ \hat{D}(0) \end{pmatrix} \tag{8.3.11}
$$

Substituting Eq. (8.3.11) into Eq. (8.3.9) and returning to fast-oscillating variables, we obtain Eqs. (8.3.4)–(8.3.6).

Problem 1.4

Find the matrix elements of the operators $\hat{a}$ and $\hat{a}^{\dagger}$ in the Fock basis.

Solution

Let us consider a 1D harmonic oscillator which Hamiltonian has the form:

$$\hat{H} = \frac{\hat{P}^2}{2m} + \frac{m\omega^2 \hat{Q}^2}{2}. \tag{8.4.1}$$

where coordinate and momentum operators satisfy the commutation relation

$$\left[\hat{Q}, \hat{P}\right] = i\hbar \tag{8.4.2}$$

It is convenient to introduce the annihilation operator $\hat{a}$ and the creation operator $\hat{a}^\dagger$ as linear combinations of the coordinate and momentum operators:

$$\hat{a} = \frac{\left(m\omega\hat{Q} + i\hat{P}\right)}{\sqrt{2m\omega\hbar}} \tag{8.4.3}$$

$$\hat{a}^\dagger = \frac{\left(m\omega\hat{Q} - i\hat{P}\right)}{\sqrt{2m\omega\hbar}} \tag{8.4.4}$$

Using Eq. (8.4.2) one can see that

$$\left[\hat{a}, \hat{a}^\dagger\right] = \hat{I} \tag{8.4.5}$$

We also have the inverse transformation:

$$\hat{Q} = \sqrt{\frac{\hbar}{2m\omega}}\left(\hat{a} + \hat{a}^\dagger\right), \qquad \hat{P} = -i\sqrt{\frac{\hbar m\omega}{2}}\left(\hat{a} - \hat{a}^\dagger\right). \tag{8.4.6}$$

In terms of operators $\hat{a}$ and $\hat{a}^\dagger$, the Hamiltonian of the harmonic oscillator can be rewritten as

$$\hat{H} = -\frac{1}{4}\hbar\omega\left(\hat{a} - \hat{a}^\dagger\right)^2 + \frac{1}{4}\hbar\omega\left(\hat{a} + \hat{a}^\dagger\right)^2 = \frac{1}{2}\hbar\omega\left(\hat{a}^\dagger\hat{a} + a\hat{a}^\dagger\right) = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\hat{I}\right) \tag{8.4.7}$$

In the last equality, we have used the identity $\hat{a}\hat{a}^\dagger = 1 + \hat{a}^\dagger\hat{a}$.

Next, we introduce the operator of the number of quanta:

$$\hat{N} = \hat{a}^\dagger\hat{a}. \tag{8.4.8}$$

Using Eq. (8.4.5), we obtain the following commutation relations for the involved operators:

$$\left[\hat{N}, \hat{a}\right] = \left[\hat{a}^\dagger\hat{a}, \hat{a}\right] = \hat{a}^\dagger\hat{a}\hat{a} - \hat{a}\hat{a}^\dagger\hat{a} = \left(\hat{a}^\dagger\hat{a} - \hat{a}\hat{a}^\dagger\right)\hat{a} = -\hat{a} \quad \text{or} \quad \hat{N}\hat{a} = \hat{a}\hat{N} - \hat{a} \tag{8.4.9}$$

$$\left[\hat{N}, \hat{a}^\dagger\right] = \hat{a}^\dagger \quad \text{or} \quad \hat{N}a^\dagger = \hat{a}^\dagger\hat{N} + \hat{a}^\dagger \tag{8.4.10}$$

For the eigenfunction of the operator $\hat{N}$, $\hat{N}|\nu\rangle = \nu|\nu\rangle$, we have:

$$\hat{N}\hat{a}|\nu\rangle = \left(\hat{a}\hat{N} - \hat{a}\right)|\nu\rangle = \hat{a}\left(\hat{N} - \hat{1}\right)|\nu\rangle = (\nu - 1)\hat{a}|\nu\rangle. \tag{8.4.11}$$

This means that if $\hat{a}|\nu\rangle \neq \hat{0}$, then $\hat{a}|\nu\rangle$ is the eigenvector of the operator $\hat{N}$ with the eigenvalue $(\nu - 1)$.

Calculating the norm of the vector $\hat{a}|\nu\rangle$

$$\langle \hat{a}\nu|\hat{a}\nu\rangle = \langle\nu|\hat{a}^{\dagger}\hat{a}|\nu\rangle = \langle\nu|\hat{N}|\nu\rangle = \nu\langle\nu|\nu\rangle \geq 0 \tag{8.4.12}$$

we see that all the eigenvalues of the operator $\hat{N}$ should be nonnegative.

After each application of the operator $\hat{a}$, we decrease the eigenvalue of the operator $\hat{N}$ by 1. At some point, we encounter a negative value; this, however, is impossible because, according to Eq. (8.4.12), $\nu \geq 0$. Therefore, to preserve the latter condition, we must assume that there is such a vector, the action of the operator $\hat{a}$ on which gives zero. We denote such a vector by $|0\rangle$

$$\hat{a}|0\rangle = |0\rangle, \quad \hat{N}|0\rangle = 0 \tag{8.4.13}$$

Similarly,

$$\hat{N}\hat{a}^{\dagger}|\nu\rangle = \left(\hat{a}^{\dagger} + \hat{a}^{\dagger}\hat{N}\right)|\nu\rangle = \hat{a}^{\dagger}\left(\hat{N} + \hat{I}\right)|\nu\rangle = (\nu + 1)\hat{a}^{\dagger}|\nu\rangle. \tag{8.4.14}$$

Calculating the norm of the vector $\hat{a}^{\dagger}|\nu\rangle$, we obtain:

$$\left\langle \hat{a}^{\dagger}\nu|\hat{a}\nu\right\rangle = \langle\nu|\hat{a}\hat{a}^{\dagger}|\nu\rangle = \langle\nu|\hat{N} + \hat{I}|\nu\rangle = (\nu + 1)\langle\nu|\nu\rangle > 0. \tag{8.4.15}$$

Thus, the vector $\hat{a}^{\dagger}|\nu\rangle$ differs from $|0\rangle$ and is the eigenvector of $\hat{N}$ with the eigenvalue $(\nu + 1)$. The application of the operator $\hat{a}^{\dagger}$ to an eigenvector obtained in the previous step turns this vector into an eigenvector whose eigenvalue is increased by 1. The first eigenvector to which the operator $\hat{a}^{\dagger}$ should be applied is $|0\rangle$, which has a zero eigenvalue. This implies that the spectrum of the operator $\hat{N}$ consists of the numbers 0, 1, 2, ... Denoting the orthonormal eigenvectors of the operator $\hat{N}$ by $|n\rangle$, we have:

$$\hat{N}|n\rangle = n|n\rangle, \quad n = 0, 1, 2, \ldots \tag{8.4.16}$$

In particular, the vector $\hat{a}^{\dagger}|\nu\rangle$ should be proportional to $|n + 1\rangle$:

$$\hat{a}^{\dagger}|n\rangle = C_n|n + 1\rangle. \tag{8.4.17}$$

The constant C_n can be obtained by taking into account

$$|C_n|^2 = \langle \hat{a}^\dagger n|\hat{a}n\rangle = (n+1)\langle n|n\rangle = (n+1). \tag{8.4.18}$$

Since the phase factor of any eigenvector of a Hermitian operator is arbitrary, then we can choose this coefficient to be real so that

$$\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle. \tag{8.4.19}$$

Using this formula, we can obtain the action of the operator $\left(\hat{a}^\dagger\right)^n$ on the vacuum vector $|0\rangle$:

$$|n\rangle = \left(\hat{a}^\dagger\right)^n|0\rangle = (n!)^{-1/2}\left(\hat{a}^\dagger\right)^n|0\rangle. \tag{8.4.20}$$

Now, we can write the matrix elements of the operator $\hat{a}^\dagger$:

$$\langle n'|\hat{a}^\dagger|n\rangle = \sqrt{n+1}\delta_{n',n+1} \tag{8.4.21}$$

Since $\hat{a}$ is the Hermitian conjugate to the operator $\hat{a}^\dagger$, its matrix is obtained from the matrix of the operator $\hat{a}^\dagger$ by the transposition and the complex conjugation:

$$\langle n'|\hat{a}|n\rangle = \sqrt{n}\delta_{n',n-1}. \tag{8.4.22}$$

Finally, we have:

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle, \quad \hat{a}|0\rangle = 0 \tag{8.4.23}$$

Problem 1.5

Find the Hamiltonian $\hat{H}^{(n-1)}$, eigenfunctions, and corresponding eigenenergies for the Jaynes-Cummings Hamiltonian:

$$\hat{H}_{JC} = \hbar\omega_{ext}\hat{a}^\dagger\hat{a} + \hbar\omega_\sigma\hat{\sigma}^\dagger\hat{\sigma} + \hbar\Omega\left(\hat{\sigma}^\dagger\hat{a} + \hat{\sigma}\hat{a}^\dagger\right) \tag{8.5.1}$$

Solution

Note that Hamiltonian (8.5.1) commutes with the operator of the total number of excitations in the system $\hat{N} = \hat{a}^\dagger\hat{a} + \hat{\sigma}^\dagger\hat{\sigma}$, i.e., $\left[\hat{H}, \hat{N}\right] = 0$. To prove this, it is sufficient to show that

$$\left[\left(\hat{\sigma}^\dagger\hat{a} + \hat{\sigma}\hat{a}^\dagger\right), \hat{a}^\dagger\hat{a} + \hat{\sigma}^\dagger\hat{\sigma}\right] = 0 \tag{8.5.2}$$

or $\left[\left(\hat{\sigma}^\dagger\hat{a} + \hat{\sigma}\hat{a}^\dagger\right), \hat{a}^\dagger\hat{a}\right] = 0$ and $\left[\left(\hat{\sigma}^\dagger\hat{a} + \hat{\sigma}\hat{a}^\dagger\right), \hat{\sigma}^\dagger\hat{\sigma}\right] = 0$.

Since the operators of TLS and EM field commute, we direct calculation of the commutators proves that. Indeed, since $\left[\left(\hat{\sigma}^\dagger\hat{a}+\hat{\sigma}\hat{a}^\dagger\right),\hat{a}^\dagger\hat{a}\right]=\left[\hat{\sigma}^\dagger\hat{a},\hat{a}^\dagger\hat{a}\right]+\left[\hat{\sigma}\hat{a}^\dagger,\hat{a}^\dagger\hat{a}\right]$ and

$$\left[\hat{\sigma}^\dagger\hat{a},\hat{a}^\dagger\hat{a}\right]=\hat{\sigma}^\dagger\hat{a}\hat{a}^\dagger\hat{a}-\hat{\sigma}^\dagger\hat{a}^\dagger\hat{a}\hat{a}=\hat{\sigma}^\dagger\hat{a}\hat{a}^\dagger\hat{a}=\hat{\sigma}^\dagger\left(\hat{a}^\dagger\hat{a}+\hat{I}\right)\hat{a}=\hat{\sigma}^\dagger\hat{a} \tag{8.5.3}$$

$$\left[\hat{\sigma}\hat{a}^\dagger,\hat{a}^\dagger\hat{a}\right]=\hat{\sigma}\hat{a}^\dagger\hat{a}^\dagger\hat{a}-\hat{a}^\dagger\hat{a}\hat{\sigma}\hat{a}^\dagger=-\hat{\sigma}\hat{a}^\dagger\left(\hat{a}\hat{a}^\dagger\right)=-\hat{\sigma}\hat{a}^\dagger\left(a^\dagger a+1\right)=-\hat{\sigma}\hat{a}^\dagger, \tag{8.5.4}$$

we can see that $\left[\left(\hat{\sigma}^\dagger\hat{a}+\hat{\sigma}\hat{a}^\dagger\right),\hat{a}^\dagger\hat{a}\right]=0$.

Similarly, we obtain $\left[\left(\hat{\sigma}^\dagger\hat{a}+\hat{\sigma}\hat{a}^\dagger\right),\hat{\sigma}^\dagger\hat{\sigma}\right]=0$. Indeed,

$$\left[\hat{\sigma}^\dagger\hat{a},\hat{\sigma}^\dagger\hat{\sigma}\right]=\hat{a}\hat{\sigma}^\dagger\hat{\sigma}^\dagger\hat{\sigma}-\hat{a}\hat{\sigma}^\dagger\hat{\sigma}\hat{\sigma}^\dagger=-\hat{a}\hat{\sigma}^\dagger\hat{\sigma}\hat{\sigma}^\dagger=\hat{a}|e\rangle\langle g||g\rangle\langle e||e\rangle\langle g|=-\hat{a}\hat{\sigma}^\dagger \tag{8.5.5}$$

$$\left[\hat{\sigma}\hat{a}^\dagger,\hat{\sigma}^\dagger\hat{\sigma}\right]=\hat{a}^\dagger\hat{\sigma}\hat{\sigma}^\dagger\hat{\sigma}-\hat{\sigma}^\dagger\hat{\sigma}\hat{\sigma}\hat{a}^\dagger=\hat{a}^\dagger\hat{\sigma}\hat{\sigma}^\dagger\hat{\sigma}=\hat{a}^\dagger|g\rangle\langle e||e\rangle\langle g||g\rangle\langle e|=\hat{a}^\dagger\hat{\sigma} \tag{8.5.6}$$

We have taken into account that $aa^\dagger=(a^\dagger a+1)$. Finally, we arrive at

$$\left[N,\hbar\Omega\left(\hat{\sigma}^\dagger\hat{a}+\hat{\sigma}\hat{a}^\dagger\right)\right]=0 \tag{8.5.7}$$

The first two terms in Eq. (8.5.1) do not change the number of excitations. The last term, as shown in Eq. (8.5.7), also does not change the number of excitations. Thus, we have $\left[\hat{H},\hat{N}\right]=0$. That means that the total number of excitations in the system conserves and the eigenstate with the energy $E_{N=n_0}$ can be searched in the following trial form:

$$\Psi_{n_0}^{JC}=c_{g,n_0}|g\rangle|n_0\rangle+c_{e,n_0-1}|e\rangle|n_0-1\rangle. \tag{8.5.8}$$

Note that $E_{|g\rangle|n_0\rangle}\neq E_{|e\rangle|n_0-1\rangle}$, but the difference between these two energies is $\hbar\Delta_\omega$. Here $|g\rangle|n_0\rangle$ corresponds to zero excitation of the atom and n_0 excitations (photons) in the mode. The total energy of this state is $n_0\hbar\omega_{ext}$. The state $|e\rangle|n_0-1\rangle$ corresponds to one excitation of atom and n_0-1 excitations (photons) in the mode. The energy of this state is $\hbar\omega_\sigma+(n_0-1)\hbar\omega_{ext}$.

To find $c_{e,\,n}$ and $c_{g,\,n}$, we should substitute Eq. (8.5.8) into the stationary Schrödinger equation:

$$\begin{aligned}\hat{H}_{JC}\Psi_{n_0}^{JC}&=\left(\hbar\omega_{ext}\hat{a}^\dagger\hat{a}+\hbar\omega_\sigma\hat{\sigma}^\dagger\hat{\sigma}+\hbar\Omega\left(\hat{\sigma}^\dagger\hat{a}+\hat{\sigma}\hat{a}^\dagger\right)\right)\left(c_{g,n_0}|g\rangle|n_0\rangle+c_{e,n_0-1}|e\rangle|n_0-1\rangle\right)\\&=\hbar\omega_{ext}\hat{a}^\dagger\hat{a}\left(c_{g,n_0}|g\rangle|n_0\rangle+c_{e,n_0-1}|e\rangle|n_0-1\rangle\right)\\&\quad+\hbar\omega_\sigma\hat{\sigma}^\dagger\hat{\sigma}\left(c_{g,n_0}|g\rangle|n_0\rangle+c_{e,n_0-1}|e\rangle|n_0-1\rangle\right)\\&\quad+\hbar\Omega\left(\hat{\sigma}^\dagger\hat{a}+\hat{\sigma}\hat{a}^\dagger\right)\left(c_{g,n_0}|g\rangle|n_0\rangle+c_{e,n_0-1}|e\rangle|n_0-1\rangle\right)\end{aligned}$$

Using

$$\hat{\sigma}^\dagger\hat{\sigma} = |e\rangle\langle e|, \quad \hat{\sigma}^\dagger|g\rangle = |e\rangle \quad \hat{\sigma}|e\rangle = |g\rangle \quad \hat{\sigma}^\dagger|e\rangle = \hat{\sigma}|g\rangle = 0$$
$$\hat{a}^\dagger\hat{a}|n\rangle = n|n\rangle \quad \hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, \quad \hat{a}|n\rangle = \sqrt{n}|n-1\rangle, \quad \hat{a}|0\rangle = 0,$$

we obtain:

$$\begin{aligned}
&\hat{a}^\dagger\hat{a}\left(c_{g,n_0}|g\rangle|n_0\rangle + c_{e,n_0-1}|e\rangle|n_0-1\rangle\right)\\
&\quad = n_0 c_{g,n_0}|g\rangle|n_0\rangle + \hbar\omega_{ext}(n_0-1)c_{e,n_0-1}|e\rangle|n_0-1\rangle\\
&\hat{\sigma}^\dagger\hat{\sigma}\left(c_{g,n_0}|g\rangle|n_0\rangle + c_{e,n_0-1}|e\rangle|n_0-1\rangle\right) = c_{e,n_0-1}|e\rangle|n_0-1\rangle\\
&\left(\hat{\sigma}^\dagger\hat{a} + \hat{\sigma}\hat{a}^\dagger\right)\left(c_{g,n_0}|g\rangle|n_0\rangle + c_{e,n_0-1}|e\rangle|n_0-1\rangle\right)\\
&\quad = \hat{\sigma}^\dagger\hat{a}\left(c_{g,n_0}|g\rangle|n_0\rangle + c_{e,n_0-1}|e\rangle|n_0-1\rangle\right)\\
&\qquad + \hat{\sigma}\hat{a}^\dagger\left(c_{g,n_0}|g\rangle|n_0\rangle + c_{e,n_0-1}|e\rangle|n_0-1\rangle\right)\\
&\quad = \hat{\sigma}^\dagger c_{e,n_0-1}|e\rangle\hat{a}|n_0-1\rangle = |e\rangle\sqrt{(n_0-1)}|n_0-2\rangle
\end{aligned}$$

Then, by using the equalities $\hat{a}|n\rangle = \sqrt{n}|n-1\rangle$, $\hat{a}^\dagger|n-1\rangle = \sqrt{n}|n\rangle$, $\hat{a}^\dagger\hat{a}|n\rangle = n|n\rangle$, $\sigma|e\rangle = |g\rangle$, $\hat{\sigma}^\dagger|g\rangle = |e\rangle$, and $\hat{\sigma}|e\rangle = |g\rangle$, we can collect the terms containing the state $|e\rangle|n_0-1\rangle$ and $|g\rangle|n_0\rangle$, where n_0 can take the values $1, 2, \ldots$. As a result, we obtain:

$$\begin{aligned}
&\left(c_{g,n_0}\hbar\omega_{ext}n_0 + c_{e,n_0-1}\hbar\Omega\sqrt{n_0}\right)|g\rangle|n_0\rangle\\
&\qquad + \left(c_{e,n_0-1}\hbar\omega_{ext}(n_0-1) + c_{e,n_0-1}\hbar\omega_\sigma + c_{g,n_0}\hbar\Omega\sqrt{n_0}\right)|e\rangle|n_0-1\rangle\\
&\quad = E_{n_0}\left(c_{g,n_0}|g\rangle|n_0\rangle + c_{e,n_0-1}|e\rangle|n_0-1\rangle\right)
\end{aligned} \tag{8.5.9}$$

From Eq. (8.5.9), we see that the Schrödinger equation

$$\hat{H}_{JC}|\psi_{JC}\rangle = E_{JC}|\psi_{JC}\rangle$$

is split into system of the two independent of equations, each of which contains either the state $|e\rangle|n_0-1\rangle$ or $|g\rangle|n_0\rangle$. Scalar multiplying Eq. (8.5.9) by the states $\langle n_0|\langle g|$, $\langle n_0|\langle e|$, and $\langle n_0-1|\langle g|$ from the left, we obtain two linear equations for the coefficients c_{g,n_0} and c_{e,n_0-1} which in the matrix form can be written as

$$\begin{pmatrix} \hbar\omega_{ext}(n_0-1)+\hbar\omega_\sigma & \hbar\Omega\sqrt{n_0} \\ \hbar\Omega\sqrt{n_0} & \hbar\omega_{ext}n_0 \end{pmatrix}\begin{pmatrix} c_{e,n_0-1} \\ c_{g,n_0} \end{pmatrix} = E_{n_0}\begin{pmatrix} c_{e,n_0-1} \\ c_{g,n_0} \end{pmatrix}. \tag{8.5.10}$$

The matrix

$$\hat{H}^{(n-1)} = \begin{pmatrix} (n-1)\hbar\omega_{ext}/2 + \hbar\omega_\sigma & \hbar\Omega\sqrt{n} \\ \hbar\Omega\sqrt{n} & n\hbar\omega_{ext} \end{pmatrix}$$

is the n_0-th diagonal cell of the total Jaynes-Cummings Hamiltonian.

The eigenenergies $E_{N=n_0}$ of the Hamiltonian are determined from the condition that there is a nontrivial solution of Eq. (8.5.10):

$$\det \begin{pmatrix} \hbar\omega_{ext} n_0 - E_{n_0} & \hbar\Omega\sqrt{n_0} \\ \hbar\Omega\sqrt{n_0} & \hbar\omega_{ext}(n_0 - 1) + \hbar\omega_\sigma - E_{n_0} \end{pmatrix} = 0 \tag{8.5.11}$$

From this equation, we obtain:

$$E_{n\pm} = \hbar\omega_{ext}(n-1) + \hbar(\omega_\sigma + \omega_{ext})/2 \pm \hbar\sqrt{\Delta^2/4 + \Omega^2 n}, \quad n \geq 1,$$

where $\Delta = \omega_{ext} - \omega_\sigma$. The corresponding normalized eigenvectors are

$$\begin{pmatrix} c_{g,n_0} \\ c_{e,n_0-1} \end{pmatrix}_+ = \begin{pmatrix} \cos\varphi_{n_0} & \sin\varphi_{n_0} \end{pmatrix}, \qquad \begin{pmatrix} c_{g,n_0} \\ c_{e,n_0-1} \end{pmatrix}_- = \begin{pmatrix} -\sin\varphi_{n_0} \\ \cos\varphi_{n_0} \end{pmatrix} \tag{8.5.12}$$

with

$$\tan(2\varphi_n) = \frac{\Omega\sqrt{n}}{\Delta/2}$$

To conclude, using Eq. (8.5.12), we can write eigenstate (8.5.8) and corresponding eigenenergy of Hamiltonian $\hat{H}_{JC}$ in the form

$$|+, n\rangle = \cos\varphi_n |e\rangle|n-1\rangle + \sin\varphi_n |g\rangle|n\rangle, \tag{8.5.13}$$

$$E_{n+} = \hbar\omega_{ext}(n-1) + \hbar(\omega_\sigma + \omega_{ext})/2 + \hbar\sqrt{(\omega_{ext} - \omega_\sigma)^2/4 + \Omega^2 n}, \tag{8.5.14}$$

and

$$|-, n\rangle = -\sin\varphi_n |e\rangle|n-1\rangle + \cos\varphi_n |g\rangle|n\rangle, \tag{8.5.15}$$

$$E_{n-} = \hbar\omega_{ext}(n-1) + \hbar(\omega_\sigma + \omega_{ext})/2 - \hbar\sqrt{(\omega_{ext} - \omega_\sigma)^2/4 + \Omega^2 n}, \tag{8.5.16}$$

for $n = 1, 2, \ldots$.

$$|g, 0\rangle, E_0 = 0 \tag{8.5.17}$$

Problem 1.6

In Sect. 3.1, it is shown that, generally, the radiation rate of an excited atom interacting with the reservoir of electromagnetic modes is described by Eq. (3.1.18), namely,

$$\gamma_D^{(rad)}/2 = \pi \sum_{\mathbf{k}} \Omega_{R,\mathbf{k}}^2 \delta(\omega_{a,\mathbf{k}} - \omega_\sigma), \tag{8.6.1}$$

and that the Lamb shift of radiation frequency is determined by Eq. (3.1.19):

$$\Delta\omega = \sum_{\mathbf{k}} \frac{\Omega_{R,\mathbf{k}}^2}{\omega_{a,\mathbf{k}} - \omega_\sigma} \tag{8.6.2}$$

Obtain the analytical formulas for these quantities for an excited atom placed into free space.

Solution

Usually, to take into account a quantized character of EM field in vacuum, the atom is considered as being placed in a resonator of the size L and the volume of quantization $V = L^3$. At the end of calculations, the volume tends to infinity, $V \to \infty$. The eigenfrequencies of the resonator are $\omega_{\mathbf{k},\,\alpha} = c|\mathbf{k}|$ and $\mathbf{k} = \frac{2\pi}{L}(m, n, l)$. The summation in Eq. (8.6.1) is performed over wave vectors and polarizations α. The coupling constants $\Omega_{\mathbf{k},\alpha} = \sqrt{\frac{2\pi\omega_{\mathbf{k}}}{\hbar V}}\mathbf{e}_{\mathbf{k},\alpha} \cdot \mathbf{d}_{eg}$ are the vacuum Rabi frequencies in the case of free space, and $\mathbf{e}_{\mathbf{k},\,\alpha}$ is the unit vector in the direction of polarization of the resonator mode.

The primitive cell of the volume in k-space is $(\Delta k)^3 = (2\pi)^3/L^3$ and $\Delta\omega = c\Delta k = c/(2\pi L)$, then in the limit $V \to \infty$, the frequency difference of the adjacent modes tends to zero, and in Eq. (8.6.1), we can replace the summation over $\mathbf{k}$ by integration using the standard summation rule:

$$\begin{aligned} \sum_{\mathbf{k},\alpha} F(\mathbf{k}) &= \sum_{\alpha} \frac{V}{(2\pi)^3} \sum_{\mathbf{k}} (\Delta k)^3 F(\mathbf{k}) \to \sum_{\alpha} \frac{V}{(2\pi)^3} \int F(\mathbf{k}) d^3\mathbf{k} \\ &= \sum_{\alpha} \frac{V}{8\pi^3 c^3} \int d\theta \sin\theta d\varphi \int F(\omega, \theta, \varphi)\omega^2 d\omega \end{aligned} \tag{8.6.3}$$

If the problem has spherical symmetry, and calculated quantity does not depend on polarization, then summation over polarization gives the factor 2, and integration over the solid angle gives the factor 4π. Thus, Eq. (8.6.3) transforms to

$$\sum_{\mathbf{k},\alpha} \to \int \frac{V\omega^2}{\pi^2 c^3} d\omega \equiv \int \Pi(\omega) d\omega \tag{8.6.4}$$

The quantity

$$\Pi(\omega) = \frac{V\omega^2}{\pi^2 c^3} \tag{8.6.5}$$

has the meaning of the density of states of free space modes of EM field.

The problem under consideration, however, depends on the polarization and does not have spherical symmetry because the Rabi interaction constant $\Omega_{\mathbf{k},\alpha} = \sqrt{2\pi\omega_{\mathbf{k}}/\hbar V}\mathbf{e}_{\mathbf{k},\alpha} \cdot \mathbf{d}_{eg}$ depends on the direction of the electric field polarization. Thus, we cannot directly use this density of states. Instead, we should perform explicit integration over solid angle and sum up over possible polarization directions the quantity $\Omega_{\mathbf{k},\,\alpha}$.

To do it, we first change the sum in Eq. (8.6.1) to the integrals over the wave vectors:

$$\pi\sum_{\mathbf{k},\,\alpha}|\Omega_{\mathbf{k},\alpha}|^2\delta(\omega_{a,\mathbf{k}} - \omega_\sigma) = \frac{\pi V}{(2\pi)^3 c}\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dk\delta(k - c\omega_\sigma)\cdot k^2 \sum_{\alpha}|\Omega_\alpha(k,\theta,\varphi)|^2 \tag{8.6.6}$$

where (φ, θ, k) are the polar coordinates in $\mathbf{k}$-space and $k = \omega/c$.

To obtain an analytical expression, we, first, perform the summation over the polarizations. For this, it is convenient to expand the vector $\mathbf{d}_{eg}$ in the basis $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{n}\}$; $\mathbf{e}_1$ and $\mathbf{e}_2$ are possible vectors of linear polarization, $\mathbf{n} = \mathbf{k}/|\mathbf{k}|$:

$$\mathbf{d} = \mathbf{e}_1\left(\mathbf{d}_{eg}\cdot\mathbf{e}_1\right) + \mathbf{e}_2\left(\mathbf{d}_{eg}\cdot\mathbf{e}_2\right) + \mathbf{n}\left(\mathbf{d}_{eg}\cdot\mathbf{n}\right), \tag{8.6.7}$$

and

$$\mathbf{d}_{eg}^2 = \left(\mathbf{d}_{eg}\cdot\mathbf{e}_1\right)^2 + \left(\mathbf{d}_{eg}\cdot\mathbf{e}_2\right)^2 + \left(\mathbf{d}_{eg}\cdot\mathbf{n}\right)^2. \tag{8.6.8}$$

If $\mathbf{d}_{eg}$ is a real vector, then

$$\left(\mathbf{d}_{eg}\cdot\mathbf{e}_1\right)^2 + \left(\mathbf{d}_{eg}\cdot\mathbf{e}_2\right)^2 = \mathbf{d}_{eg}^2 - \left(\mathbf{d}_{eg}\cdot\mathbf{n}\right)^2 = \mathbf{d}_{eg}^2\sin^2\theta, \tag{8.6.9}$$

where θ is the angle between $\mathbf{d}_{eg}$ and $\mathbf{n}$. Taking into account Eq. (8.6.9), the integration in Eq. (8.6.6) is reduced to the following integral:

$$\frac{V}{(2\pi)^3 c}\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dk\cdot k^2\delta(k - c\omega_\sigma)|\Omega(k,\theta,\varphi)|^2 \tag{8.6.10}$$

where the square of the Rabi constant is

$$|\Omega(k,\theta,\varphi)|^2 = \frac{2\pi ck}{\hbar V}\mathbf{d}_{eg}^2 \sin^2\theta \tag{8.6.11}$$

Integral (8.6.10) can be calculated explicitly:

$$\begin{aligned}&\frac{\pi V}{(2\pi)^3 c}\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \int_0^{\infty} dk \cdot k^2 \delta(k-\omega_\sigma/c)\frac{2\pi ck}{\hbar V}\mathbf{d}_{eg}^2 \sin^2\theta \\ &= \frac{\mathbf{d}_{eg}^2}{2\hbar c^3}\int_0^{\pi} d\theta \sin^3\theta \int_0^{\infty} d\omega\omega^3\delta(\omega-\omega_\sigma) = \int_0^{\infty} d\omega \frac{2\mathbf{d}_{eg}^2\omega^3}{3\hbar c^3}\delta(\omega-\omega_\sigma) = \frac{2\mathbf{d}_{eg}^2\omega_\sigma^3}{3\hbar c^3}\delta(\omega-\omega_\sigma)\end{aligned} \tag{8.6.12}$$

From Eqs. (8.6.1) and (8.6.12), we obtain:

$$\gamma_D^{(rad)} = \frac{4}{3}\frac{\left|\mathbf{d}_{eg}\right|^2\omega_\sigma^3}{\hbar c^3}. \tag{8.6.13}$$

Note that by using Eq. (8.6.5), Equation (8.6.13) can be written in the form:

$$\begin{aligned}\gamma_D^{(rad)} &= \int_0^{\infty} d\omega \frac{4\mathbf{d}_{eg}^2\omega^3}{3\hbar c^3}\delta(\omega-\omega_\sigma) = \int_0^{\infty} d\omega \frac{4\mathbf{d}_{eg}^2\omega^3}{3\hbar c^3|\Omega(\omega)|^2\Pi(\omega)}\Pi(\omega)|\Omega(\omega)|^2\delta(\omega-\omega_\sigma) \\ &= \int_0^{\infty} d\omega \frac{2\pi}{3}\Pi(\omega)|\Omega(\omega)|^2\delta(\omega-\omega_\sigma),\end{aligned} \tag{8.6.14}$$

where $\Omega(\omega) = \sqrt{2\pi\omega\mathbf{d}_{eg}^2/\hbar V}$ is the Rabi constant obtained after the summation over polarizations and the integration over angles, and which depends only on the frequency.

Calculations for the frequency shift (8.6.2) give:

$$\Delta\omega = \mathcal{P}\int d\omega \frac{1}{3}\frac{\Pi(\omega)\Omega^2(\omega)}{\omega-\omega_\sigma} = \frac{2\left|\mathbf{d}_{eg}\right|^2\omega_\sigma^3}{3\pi\hbar c^3}\int_0^{\infty}\mathcal{P}\left(\frac{1}{\omega-\omega_{TLS}}\right)d\omega \tag{8.6.15}$$

This value is the Lamb shift of the TLS transition frequency. This shift arises due to the interaction of the TLS with vacuum fluctuations of free space modes. Formally, integral (8.6.15) diverges. The physical meaning of this divergence is caused by the

inapplicability of the nonrelativistic Jaynes-Cummings Hamiltonian at high frequencies, when photons emitted by the TLS are capable of producing virtual electron-positron pairs with energy $\hbar\omega_{\mathbf{k}} \approx 2mc^2$, where m is the electron mass. An accurate calculation of the Lamb shift $\Delta_L\omega$ can be carried out only by QED methods, taking into account relativistic and radiative corrections.

However, evaluation of $\Delta_L\omega$ can be obtained by cutting off integral (8.6.15) at the frequency $\omega \approx \hbar^{-1}2mc^2$. Such a procedure gives:

$$\Delta\omega = \frac{2\left|\mathbf{d}_{eg}\right|^2\omega_\sigma^3}{3\pi\hbar c^3}\ln\left(\frac{2mc^2}{\hbar\omega_\sigma}\right). \tag{8.6.16}$$

The resulting expression differs only by a numerical factor from the QED prediction. Note that the Lamb shift, $\Delta\omega \sim \gamma_D^{(rad)} \ll \omega_\sigma$, is in the microwave frequency range.

Problem 1.7
Prove that the relation from Sect. 3.2.2

$$\mathrm{Tr}_R\left(\hat{\rho}_R^{th}\widehat{\widetilde{R}}(t_1)\right) = 0 \tag{8.7.1}$$

Solution
The Hamiltonian $\hat{H}_R$ of the reservoir of free space EM modes can be presented as a sum of independent Hamiltonians of harmonic oscillators (see Sect. 2.5):

$$\hat{H}_R = \sum_k \hat{H}_{Rk} = \sum_k \hbar\omega_k \hat{a}_k^+\hat{a}_k, \quad \hat{H}_{Rk} = \hbar\omega_k\hat{a}_k^+\hat{a}_k. \tag{8.7.2}$$

We assume that the reservoirs are in thermal equilibrium; consequently, the density matrix of the reservoir has the form $\hat{\rho}_R^{th} = \exp\left(-\hat{H}_R/kT\right)/\mathrm{Tr}\left(\exp\left(-\hat{H}_R/kT\right)\right)$. Since the Hamiltonian (8.7.2) is Hermitian, the basis $\{|n_k\rangle\}$ comprised of its eigenstates is complete, $\hat{I} = \sum\limits_{n_k=0}^{\infty}|n_k\rangle\langle n_k|$. Thus, the density matrix $\hat{\rho}_R^{th}$ can be presented as

$$\begin{aligned}
\hat{\rho}_R^{th} &= \exp\left(-\hat{H}_R/kT\right)/\mathrm{Tr}\left(\exp\left(-\hat{H}_R/kT\right)\right) = \hat{I}\frac{\exp\left(-\sum\limits_k \hbar\omega_{a,\mathbf{k}}\hat{a}_k^+\hat{a}_k/kT\right)}{\mathrm{Tr}\left(\exp\left(-\hat{H}_R/kT\right)\right)}\hat{I} \\
&= \hat{I}\frac{\prod\limits_k \exp\left(-\hbar\omega_{a,\mathbf{k}}\hat{a}_k^+\hat{a}_k/kT\right)}{\mathrm{Tr}\left(\exp\left(-\hat{H}_R/kT\right)\right)}\hat{I} = \frac{\prod\limits_k \hat{1}\exp\left(-\hbar\omega_{a,\mathbf{k}}\hat{a}_k^+\hat{a}_k/kT\right)\hat{I}}{\mathrm{Tr}\left(\exp\left(-\hat{H}_R/kT\right)\right)} \\
&= \frac{\prod\limits_k \sum\limits_{n_k=0}^{\infty}\exp(-\hbar\omega_{a,k}n/kT)|n_k\rangle\langle n_k|}{\mathrm{Tr}\left(\exp\left(-\hat{H}_R/kT\right)\right)}
\end{aligned} \tag{8.7.3}$$

The operator $\hat{R} = \frac{1}{\Omega_a(\omega_\sigma)} \sum_k \sqrt{\frac{2\pi\hbar\omega_{a,k}}{V}} \left(\hat{a}_k^\dagger + \hat{a}_k\right)$ is a part of the interaction Hamiltonian that depends on the degrees of freedom of the reservoir of the free space modes (see Sect. 3.2.3). This operator in the interaction picture is

$$\begin{aligned} \widehat{\widehat{R}}(t) = \exp\left(i\hat{H}_R t\right)\hat{R}\exp\left(-i\hat{H}_R t\right) = \frac{1}{\Omega_a(\omega_\sigma)} \sum_k \sqrt{\frac{2\pi\hbar\omega_{a,k}}{V}} \\ \times \left(\hat{a}_k^\dagger \exp(-i\omega_k t) + \hat{a}_k \exp(i\omega_k t)\right). \end{aligned} \tag{8.7.4}$$

From Eqs. (8.7.3) and (8.7.4), we obtain:

$$\begin{aligned} \mathrm{Tr}_R\left(\hat{\rho}_R^{th}\widehat{\widehat{R}}(t_1)\right) = \frac{1}{\Omega_a(\omega_\sigma)} \sum_k \sqrt{\frac{2\pi\hbar\omega_{a,k}}{V}} \left(\mathrm{Tr}\left(\exp(-\hbar\omega_k n/kT)|n\rangle\langle n|\hat{a}_k^\dagger\right)\right. \\ \left. \exp(-i\omega_k t) + \mathrm{Tr}(\exp(-\hbar\omega_k n/kT)|n\rangle\langle n|\hat{a}_k)\exp(i\omega_k t)\right) = 0 \end{aligned} \tag{8.7.5}$$

The Hamiltonian of the dephasing reservoir is (see Sect. 3.2.3)

$$\hat{H}_R = \sum_n \hbar\omega_n^{dp} \hat{c}_n^{dp\dagger} \hat{c}_n^{dp}, \tag{8.7.6}$$

The operator $\hat{R}$ of the TLS interaction with the dephasing reservoir is $\hat{R} = \sum_n \kappa_n \left(\hat{c}_n^{dp\dagger} + \hat{c}_n^{dp}\right) / \sum_n \kappa_n$ (see Sect. 3.2.3). This operator in the interaction picture is

$$\widehat{\widehat{R}}(t) = \exp\left(i\hat{H}_R t\right)\hat{R}\exp\left(-i\hat{H}_R t\right) = \sum_n \kappa_n \left(\hat{c}_n^{dp\dagger}\exp(-i\omega_n t) + \hat{c}_n^{dp}\exp(i\omega_n t)\right) / \sum_n \kappa_n, \tag{8.7.7}$$

From Eqs. (8.7.3) and (8.7.4), we obtain:

$$\begin{aligned} \mathrm{Tr}_R\left(\hat{\rho}_R^{th}\widehat{\widehat{R}}(t_1)\right) = \frac{1}{\sum_n \kappa_n} \sum_n \kappa_n \left(\mathrm{Tr}\left(\exp(-\hbar\omega_k n/kT)|n\rangle\langle n|\hat{c}_k^\dagger\right)\right. \\ \left. \exp(-i\omega_k t) + +\mathrm{Tr}(\exp(-\hbar\omega_k n/kT)|n\rangle\langle n|\hat{c}_k)\exp(i\omega_k t)\right) = 0. \end{aligned}$$

Problem 1.8
Prove the Kubo-Martin-Schwinger formula (3.2.25):

$$\gamma_{k'k''}/\gamma_{k''k'} = \exp(\hbar\Delta\omega_{k'k''}/kT),$$

where $\gamma_{k'k''}/2=\kappa^2 f(\Delta\omega_{k'k''})\left|\langle k'|\hat{S}|k''\rangle\right|^2$, $K(t_1-t_2)=Tr_R\left(\widehat{\widehat{R}}(t_2)\widehat{\widehat{R}}(t_1)\hat{\rho}_R\right)$ (see Eq. 3.2.22) and $\int\limits_{t_0-t_1}^{t_0+\Delta t-t_1} d\tau\kappa^2\exp\left(i\Delta\omega_{k'''k''''}\tau\right)K(\tau)\approx\int\limits_{-\infty}^{\infty}\kappa^2\exp\left(i\Delta\omega_{k'''k''''}\tau\right)K(\tau)d\tau\equiv\kappa^2 f\left(\Delta\omega_{k'''k''''}\right)$ (see Eq. 3.2.20).

Solution

In the main text, for the dissipation rate $\gamma(\Delta\omega_{k'k''})\equiv\gamma_{k'k''}$ (where $\Delta\omega_{k'k''}$ is the frequency difference between levels $|k'\rangle$ and $|k''\rangle$), the following equation has been obtained:

$$\gamma_{k'k''}/2=\kappa^2\left|\langle k'|\hat{S}|k''\rangle\right|^2\int\limits_{-\infty}^{\infty}\exp(i\Delta\omega_{k'k''}\tau)Tr_R\left(\widehat{\widehat{R}}(t+\tau)\widehat{\widehat{R}}(t)\hat{\rho}_R\right)d\tau \tag{8.8.1}$$

For definiteness, we suppose that $\Delta\omega_{k'k''}\equiv\Delta\omega>0$. Recall that $\hat{S}$ is the Hermitian operator, which acts on the system variables and determines the interaction, $\hat{H}_{SR}=\hbar\kappa\hat{S}\hat{R}$ (Eq. (3.2.7)), between the system and the reservoir. Thus, $\left|\langle k'|\hat{S}|k''\rangle\right|^2=\left|\langle k''|\hat{S}|k'\rangle\right|^2$. As a consequence, we have:

$$\frac{\gamma(\Delta\omega)}{\gamma(-\Delta\omega)}=\frac{\int\limits_{-\infty}^{\infty}\exp(i\Delta\omega\tau)Tr_R\left(\widehat{\widehat{R}}(t+\tau)\widehat{\widehat{R}}(t)\hat{\rho}_R\right)d\tau}{\int\limits_{-\infty}^{\infty}\exp(-i\Delta\omega\tau)Tr_R\left(\widehat{\widehat{R}}(t+\tau)\widehat{\widehat{R}}(t)\hat{\rho}_R\right)d\tau} \tag{8.8.2}$$

In all cases considered in the book, it is assumed that the reservoir consists of bosonic modes. It is also assumed that the operator $\hat{R}$, which acts on the reservoir variables and determines the interaction, $\hat{H}_{SR}=\hbar\kappa\hat{S}\hat{R}$, between the reservoir and the system, has the form $\hat{R}=\sum_n\gamma_n\left(\hat{a}_n+\hat{a}_n^\dagger\right)$, where a_n and $\hat{a}_n^\dagger$ are annihilation and creation operators for the n-th mode of the reservoir and γ_n is the dimensionless coupling constant. The Hamiltonian of the reservoir of bosonic modes has the form:

$$\hat{H}_R=\hbar\sum_n\omega_n\hat{a}_n^\dagger\hat{a}_n \tag{8.8.3}$$

The interaction operator in the interaction picture can be calculated explicitly:

$$\begin{aligned}\widehat{\widehat{R}}(t)&=\exp\left(it\sum_{n_1}\omega_{n_1}\hat{a}_{n_1}^\dagger\hat{a}_{n_1}\right)\sum_n\gamma_n\left(\hat{a}_n+\hat{a}_n^\dagger\right)\exp\left(-it\sum_{n_2}\omega_{n_2}\hat{a}_{n_2}^\dagger\hat{a}_{n_2}\right)\\&=\sum_n\gamma_n\left(\exp\left(i\omega_n t\hat{a}_n^\dagger\hat{a}_n\right)\hat{a}_n\exp\left(-i\omega_n t\hat{a}_n^\dagger\hat{a}_n\right)+\exp\left(i\omega_n t\hat{a}_n^\dagger\hat{a}_n\right)\hat{a}_n^\dagger\exp\left(i\omega_n t\hat{a}_n^\dagger\hat{a}_n\right)\right)\\&=\sum_n\gamma_n\left(\hat{a}_n\exp(-i\omega_n t)+\hat{a}_n^\dagger\exp(i\omega_n t)\right)\end{aligned} \tag{8.8.4}$$

where we use commutation relations for bosonic modes $\left[\hat{a}_{n_1}\hat{a}_{n_2}^{\dagger}\right]=\delta_{n_1,n_2}\hat{1}$ and equalities $\exp\left(i\omega_n t\hat{a}_n^{\dagger}\hat{a}_n\right)\hat{a}_n\exp\left(-i\omega_n t\hat{a}_n^{\dagger}\hat{a}_n\right)=\hat{a}_n\exp(-i\omega_n t)$ and $\exp\left(i\omega_n t\hat{a}_n^{\dagger}\hat{a}_n\right)\hat{a}_n^{\dagger}\exp\left(-i\omega_n t\hat{a}_n^{\dagger}\hat{a}_n\right)=\hat{a}_n^{\dagger}\exp(i\omega_n t)$.

Using Eq. (8.8.4), for the numerator of Eq. (8.8.2), we obtain:

$$\begin{aligned}
&\int_{-\infty}^{\infty}\exp(i\Delta\omega\tau)\mathrm{Tr}_R\left(\widehat{\widetilde{R}}(t+\tau)\widehat{\widetilde{R}}(t)\hat{\rho}_R\right)d\tau\\
&=\sum_{n_1,n_2}\gamma_{n_1}\gamma_{n_2}\int_{-\infty}^{\infty}d\tau\exp(i\Delta\omega\tau)\left(\langle\hat{a}_{n_1}\hat{a}_{n_2}\rangle e^{-i\left(\omega_{n_1}(t+\tau)+\omega_{n_2}t\right)}+\left\langle\hat{a}_{n_1}^{\dagger}\hat{a}_{n_2}^{\dagger}\right\rangle e^{i\left(\omega_{n_1}(t+\tau)+\omega_{n_2}t\right)}\right)\\
&+\sum_{n_1,n_2}\gamma_{n_1}\gamma_{n_2}\int_{-\infty}^{\infty}d\tau\exp(i\Delta\omega\tau)\left(\left\langle\hat{a}_{n_1}^{\dagger}\hat{a}_{n_2}\right\rangle e^{i\left(\omega_{n_1}(t+\tau)-\omega_{n_2}t\right)}+\left\langle\hat{a}_{n_1}\hat{a}_{n_2}^{\dagger}\right\rangle e^{-i\left(\omega_{n_1}(t+\tau)-\omega_{n_2}t\right)}\right)
\end{aligned}\tag{8.8.5}$$

We suppose that the reservoir is in the thermal equilibrium, therefore, $\langle\hat{a}_{n_1}\hat{a}_{n_2}\rangle=\left\langle\hat{a}_{n_1}^{\dagger}\hat{a}_{n_2}^{\dagger}\right\rangle=0$ and $\left\langle\hat{a}_{n_1}^{\dagger}\hat{a}_{n_2}\right\rangle=\overline{n}_{n_1}\delta_{n_1,n_2}$, $\left\langle\hat{a}_{n_1}\hat{a}_{n_2}^{\dagger}\right\rangle=(\overline{n}_{n_1}+1)\delta_{n_1,n_2}$ where $\overline{n}_{n_1}$ is the mean number of quanta in the mode n_1. Passing from summation over n to integration over τ, we see that the first two terms on the right-hand side of Eq. (8.8.5) equal to zero. Then, we obtain:

$$\begin{aligned}
&\int_{-\infty}^{\infty}\exp(i\Delta\omega\tau)Tr_R\left(\widehat{\widetilde{R}}(t+\tau)\widehat{\widetilde{R}}(t)\hat{\rho}_R\right)d\tau\\
&=\sum_n|\gamma_n|^2\int_{-\infty}^{\infty}d\tau\exp(i\Delta\omega\tau)\left(\overline{n}_n e^{i\omega_n\tau}+(\overline{n}_n+1)e^{-i\omega_n\tau}\right)\\
&=2\pi\sum_n|\gamma_n|^2(\overline{n}_n\delta(\omega_n+\Delta\omega)+(\overline{n}+1)\delta(\omega_n-\Delta\omega))=\\
&=2\pi\int_0^{\infty}d\omega\Pi(\omega)\left(|\gamma(\omega)|^2(\overline{n}(\omega)\delta(\omega+\Delta\omega)+(\overline{n}(\omega)+1)\delta(\omega-\Delta\omega))\right)\\
&=2\pi\Pi(\Delta\omega)|\gamma(\Delta\omega)|^2(\overline{n}(\Delta\omega)+1)
\end{aligned}\tag{8.8.6}$$

Here we use the density of the reservoir states $\Pi(\omega)$ to move from summation to integration over frequencies. In Eq. (8.8.6), $\overline{n}(\omega)=\left(e^{\hbar\omega/kT}-1\right)^{-1}$ is the number of quanta in the modes with the frequency ω which, for bosonic reservoir, obeys Bose-Einstein distribution.

Similarly, for the denominator of Eq. (8.8.2), we obtain:

$$\int_{-\infty}^{\infty} \exp(-i\Delta\omega\tau) Tr_R\left(\widehat{\widetilde{R}}(t+\tau)\widehat{\widetilde{R}}(t)\hat{\rho}_R\right) d\tau = 2\pi\Pi(\Delta\omega)|\gamma(\omega)|^2\overline{n}(\Delta\omega)$$

And finally,

$$\frac{\gamma(\Delta\omega)}{\gamma(-\Delta\omega)} = \frac{\overline{n}(\Delta\omega)+1}{\overline{n}(\Delta\omega)} = \exp(\hbar\Delta\omega/kT)$$

Problem 1.9
In the Schrödinger picture, derive the form of a two-time correlator of the product of the Heisenberg operators $\langle \hat{A}_H(t+\tau)\hat{B}_H(t)\rangle_S$ where $\hat{A}$ and $\hat{B}$ are the operators of a system that interacts with a reservoir.

Solution
First, we consider the properties of the solution to the Lindblad equation. We start from the initial density matrix in the form:

$$\hat{\rho}(0) = \hat{\rho}_S(0) \otimes \hat{\rho}_R^{th}, \tag{8.9.1}$$

where $\hat{\rho}_S(t)$ is the system density matrix; $\hat{\rho}_R^{th} = \exp\left(-\hat{H}_R/kT\right)$ is the density matrix of the reservoir, which is in thermal equilibrium; and $\otimes$ denotes the direct product of matrices. In the Schrödinger picture, the total density matrix $\rho(t)$ satisfies the von Neumann equation:

$$\frac{\partial\hat{\rho}}{\partial t} = -\frac{1}{i\hbar}\left[\left(\hat{H}_S + \hat{H}_R + \hat{H}_{SR}\right), \rho\right],$$

and therefore, it can be presented as

$$\rho(t) = \exp\left(-i\left(\hat{H}_S + \hat{H}_R + \hat{H}_{SR}\right)t\right)\left(\hat{\rho}_S(0) \otimes \hat{\rho}_R^{th}\right)\exp\left(i\left(\hat{H}_S + \hat{H}_R + \hat{H}_{SR}\right)t\right). \tag{8.9.2}$$

In the framework of the Born-Markov approximation, we assume that the reservoir is in thermal equilibrium and its density matrix obeys Gibbs distribution. For the system density matrix, we obtain the Lindblad master equation, which takes into account dissipation due to interaction with the reservoir through the interaction Hamiltonian $\hat{H}_{SR} = \hbar\kappa\hat{S}\hat{R}$ (see Eq. (3.2.7) from Sect. 3.2 and the discussion following this equation). This means that the density matrix of the system and reservoir has the form:

$$\rho(t) = \hat{\rho}_S(t) \otimes \rho_R^{th} = \left(\hat{P}_L(t;0)[\hat{\rho}_S(0)]\right) \otimes \rho_R^{th}, \tag{8.9.3}$$

where $\hat{P}_L(t_2;t_1)$ is the propagator of the Lindblad master equation. In the Born approximation, the reservoir density matrix is constant, and we can use Eq. (8.9.3). Moreover, in this approximation, we suppose that Eqs. (8.9.3) and (8.9.2) are equivalent (see Sect. 3.2 of Part I), i.e.,

$$e^{\left(-i\left(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\right)t\right)}\left(\hat{\rho}_S(0)\otimes\hat{\rho}_R^{th}\right)e^{\left(i\left(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\right)t\right)}\approx\left(\hat{P}(t;0)[\hat{\rho}_S(0)]\right)\otimes\rho_R^{th}. \quad (8.9.4)$$

In Sect. 3.2, we show that this approach is valid with the accuracy κ^2 where κ describes the interaction of the system with the reservoir (see Eq. (3.2.7) from the main text) and on the time scale $t \gg 1/\Delta\omega_S$.

In the Heisenberg picture, the correlator $\left\langle\hat{A}_H(t+\tau)\hat{B}_H(t)\right\rangle$ is defined through the density matrix $\left\langle\hat{A}_H(t+\tau)\hat{B}_H(t)\right\rangle=\mathrm{Tr}\left(\hat{A}_H(t+\tau)\hat{B}_H(t)\hat{\rho}_H\right)$, where $\hat{\rho}_H$ does not depend on time and is defined as $\hat{\rho}_H=\hat{\rho}_{Schr}(0)$. The operators in the Heisenberg picture are related to the operators in the Schrödinger picture as (see Eq. (2.1.5)):

$$\hat{A}_H(t)=\exp\left(i\hat{H}t\right)\hat{A}_{Schr}\exp\left(-i\hat{H}t\right),\quad \hat{B}_H(t)=\exp\left(i\hat{H}t\right)\hat{B}_{Schr}\exp\left(-i\hat{H}t\right) \quad (8.9.5)$$

and

$$\hat{\rho}_{Schr}(t)=\exp\left(-i\hat{H}t\right)\hat{\rho}_{Schr}(0)\exp\left(i\hat{H}t\right), \quad (8.9.6)$$

where $\hat{H}$ is the Hamiltonian of the closed system.

Thus, in the Schrödinger picture, the expression $\left\langle\hat{A}(t+\tau)\hat{B}(t)\right\rangle=\mathrm{Tr}\left(\hat{A}_H(t+\tau)\hat{B}_H(t)\hat{\rho}_H\right)$ looks as

$$\begin{aligned}
&\mathrm{Tr}\left(\hat{A}_H(t+\tau)\hat{B}_H(t)\hat{\rho}_H\right)=\\
&\quad=\mathrm{Tr}_{S+R}\left[\exp\left(i\left(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\right)(\tau)\right)\hat{A}_{Schr}\exp\left(-i\left(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\right)\tau\right)\right.\\
&\qquad\left.\times\hat{B}_{Schr}\exp\left(-i\left(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\right)t\right)\left(\hat{\rho}_S(0)\otimes\hat{\rho}_R^{th}\right)\exp\left(i\left(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\right)t\right)\right]\\
&\quad=\mathrm{Tr}_{S+R}\left[\exp\left(i\left(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\right)(\tau)\right)\hat{A}_{Schr}\exp\left(-i\left(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\right)\tau\right)\right.\\
&\qquad\left.\times\hat{B}_{Schr}\left(\hat{\rho}_S(t)\otimes\hat{\rho}_R^{th}\right)\right]
\end{aligned} \quad (8.9.7)$$

Employing the Born-Markov approximation, in the framework of which we have Eq. (8.9.4), we substitute the latter equation into Eq. (8.9.7) and obtain:

$$\begin{aligned}
&\mathrm{Tr}\left(\hat{A}_H(t+\tau)\hat{B}_H(t)\hat{\rho}_H\right)\\
&\quad\approx\mathrm{Tr}_{S+R}\left[\exp\left(i\left(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\right)(\tau)\right)\hat{A}_{Schr}\exp\left(-i\left(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\right)\tau\right)\right.\\
&\qquad\left.\times\hat{B}_{Schr}\left(\hat{V}(t;0)[\rho_S(0)]\right)\otimes\rho_R^{th}\right]
\end{aligned} \quad (8.9.8)$$

If the operators $\hat{A}_{Schr}$ and $\hat{B}_{Schr}$ act only on the system variables but not on the reservoir ones, they can be presented as

$$\hat{A}_{Schr} = \hat{A}_S \otimes \hat{1}_R, \quad \hat{B}_{Schr} = \hat{B}_S \otimes \hat{1}_R \tag{8.9.9}$$

Using Eq. (8.9.9), we can rewrite Eq. (8.9.8) in the following form:

$$\begin{aligned}&\mathrm{Tr}\big(\hat{A}_H(t+\tau)\hat{B}_H(t)\hat{\rho}_H\big)\\ &\quad\approx \mathrm{Tr}_{S+R}\big[\exp\big(i\big(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\big)(\tau)\big)\big(\hat{A}_S\otimes\hat{1}_R\big)\exp\big(-i\big(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\big)\tau\big)\\ &\quad\times\big(\hat{B}_S\otimes\hat{1}_R\big)\big(\hat{V}(t;0)[\rho_S(0)]\big)\otimes\rho_R^{th}\big)\big].\end{aligned} \tag{8.9.10}$$

Using the equality $\big(\hat{P}_S\otimes\hat{Q}_R\big)\big(\hat{M}_S\otimes\hat{N}_R\big)=\hat{P}_S\hat{M}_S\otimes\hat{Q}_R\hat{N}_R$ (see, e.g., [Horn, R. A., & Johnson, C. R. (2012). Matrix analysis. Cambridge university press]), where $\hat{P}_S,\hat{M}_S$ are any system operators and $\hat{Q}_R,\hat{N}_R$ are any reservoir operators. Using this property, Eq. (8.9.10) takes the form:

$$\begin{aligned}&\mathrm{Tr}\big(\hat{A}_H(t+\tau)\hat{B}_H(t)\hat{\rho}_H\big)\\ &\quad\approx \mathrm{Tr}_{S+R}\big[\exp\big(i\big(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\big)(\tau)\big)\big(\hat{A}_S\otimes\hat{1}_R\big)\exp\big(-i\big(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\big)\tau\big)\\ &\quad\times\big(\hat{B}_S\hat{V}(t;0)[\rho_S(0)]\big)\otimes\rho_R^{th}\big]\\ &\quad=\mathrm{Tr}_{S+R}\big[\big(\hat{A}_S\otimes\hat{1}_R\big)\exp\big(-i\big(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\big)\tau\big)\times\big(\big(\hat{B}_S\hat{V}(t;0)[\rho_S(0)]\big)\otimes\rho_R^{th}\big)\\ &\qquad\exp\big(i\big(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\big)(\tau)\big)\big]\end{aligned} \tag{8.9.11}$$

In the last step, we use the invariance of the trace with respect to cyclic permutations. Note that according to Eq. (8.9.4)

$$\begin{aligned}&\exp\big(-i\big(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\big)(t+\tau)\big)\big(\big(\hat{B}_S\hat{V}(t;0)[\rho_S(0)]\big)\otimes\rho_R^{th}\big)\\ &\exp\big(i\big(\hat{H}_S+\hat{H}_R+\hat{H}_{SR}\big)\tau\big)\approx\hat{V}(t+\tau;t)\big[\big(\hat{B}_S\hat{V}(t;0)[\rho_S(0)]\big)\big]\otimes\rho_R^{th}\end{aligned} \tag{8.9.12}$$

Substituting Eq. (8.9.12) into Eq. (8.9.11) gives:

$$\begin{aligned}&\mathrm{Tr}\big(\hat{A}_H(t+\tau)\hat{B}_H(t)\hat{\rho}_H\big)\\ &\quad\approx\mathrm{Tr}_{S+R}\big(\big(\hat{A}_S\otimes\hat{1}_R\big)\hat{V}(t+\tau;t)\big[\big(\hat{B}_S\hat{V}(t;0)[\rho_S(0)]\big)\big]\otimes\rho_R^{th}\big)\\ &\quad=\mathrm{Tr}_{S+R}\big(\hat{A}_S\hat{V}(t+\tau;t)\big[\big(\hat{B}_S\hat{V}(t;0)[\rho_S(0)]\big)\big]\otimes\rho_R^{th}\big)\\ &\quad=\mathrm{Tr}_S\big(\hat{A}_S\hat{V}(t+\tau;t)\big[\big(\hat{B}_S\hat{V}(t;0)[\rho_S(0)]\big)\big]\big)\mathrm{Tr}_R\big(\rho_R^{th}\big)\\ &\quad=\mathrm{Tr}_S\big(\hat{A}_S\hat{V}(t+\tau;t)\big[\big(\hat{B}_S\hat{V}(t;0)[\rho_S(0)]\big)\big]\big)\end{aligned} \tag{8.9.13}$$

In Eq. (8.9.13) we use that $\mathrm{Tr}_{S+R}\big(\hat{P}_S\otimes\hat{Q}_R\big)=\mathrm{Tr}_S\big(\hat{P}_S\big)\mathrm{Tr}_R\big(\hat{Q}_R\big)$ and that $\mathrm{Tr}_R\big(\rho_R^{th}\big)=1$.

Problem 1.10

Show that the noise terms in the Heisenberg-Langevin equations for operators $\hat{\sigma}$, $\hat{\sigma}^{\dagger}$, $\hat{D}$ for an atom in free space

$$\frac{d\hat{\sigma}(t)}{dt} = \left(-i\omega_{\sigma} - \gamma_D^{(rad)}/2\right)\hat{\sigma}^{\dagger}(t) + \hat{F}_{\sigma}(t) \tag{8.10.1}$$

$$\frac{d\hat{\sigma}^{\dagger}(t)}{dt} = \left(i\omega_{\sigma} - \gamma_D^{(rad)}/2\right)\hat{\sigma}^{\dagger}(t) + \hat{F}_{\sigma^{\dagger}}(t) \tag{8.10.2}$$

$$\frac{d\hat{D}(t)}{dt} = -\gamma_D^{(rad)}\hat{D}(t) + \hat{F}_D(t) \tag{8.10.3}$$

have the following correlation properties

$$\left\langle \hat{F}_i(t) \right\rangle = 0, \tag{8.10.4}$$

$$\left\langle \hat{F}_i(t+\tau)\hat{F}_j(t) \right\rangle = 2M_{ij}\delta(\tau), \quad i,j = \left\{\sigma, \sigma^{\dagger}, D\right\}, \tag{8.10.5}$$

with

$$M_{ij} = \gamma_D^{(rad)} \begin{pmatrix} \overline{n}(\omega_{\sigma})/2 & 0 & -\overline{n}(\omega_{\sigma})\hat{\sigma}^{\dagger}(t) \\ 0 & (\overline{n}(\omega_{\sigma})+1)/2 & (\overline{n}(\omega_{\sigma})+1)\hat{\sigma}(t) \\ -\overline{n}(\omega_{\sigma})\hat{\sigma}(t) & (\overline{n}(\omega_{\sigma})+1)\hat{\sigma}^{\dagger}(t) & \overline{n}(\omega_{\sigma})\left(1-\hat{D}\right) + (\overline{n}(\omega_{\sigma})+1)\left(1+\hat{D}\right) \end{pmatrix} \tag{8.10.6}$$

Solution

As we show in Sect. 3.4, in the dipole approximation, the Hamiltonian of the interaction of the TLS with the reservoir of free space electromagnetic modes can be written as

$$\hat{H} = \hbar\omega_{\sigma}\hat{\sigma}^{\dagger}\hat{\sigma} + \hbar\sum_k \omega_k \hat{a}_k^{\dagger}\hat{a}_k + \hbar\sum_k \Omega_k \left(\hat{a}_k^{\dagger}\hat{\sigma} + \hat{\sigma}^{\dagger}\hat{a}_k\right) \tag{8.10.7}$$

Here $\hat{a}_k$ and $\hat{a}_k^{\dagger}$ are operators of annihilation and creation of the mode with the wave vector k and frequency ω_k; $\Omega_k = -\mathbf{d}_{\mathrm{TLS}} \cdot \mathbf{E}_k/\hbar$ is the coupling constant of the TLS dipole moment $\mathbf{d}_{\mathrm{TLS}}$ and the k-th mode electric of the field $\mathbf{E}_k$. Recall that $\hat{\mathbf{d}} = \mathbf{d}_{eg}\left(\hat{\sigma} + \hat{\sigma}^{\dagger}\right)$ (Sect. 2.1, Eq. (2.3.23)).

Using the Heisenberg equation

$$\frac{d\hat{A}}{dt} = \frac{\partial\hat{A}}{\partial t} + \frac{i}{\hbar}\left[\hat{H}, \hat{A}\right],$$

we can obtain the Heisenberg equations for the operators of the TLS dipole moment $\hat{\sigma}$, the TLS inversion $\hat{D} = \hat{\sigma}^{\dagger}\hat{\sigma} - \hat{\sigma}\hat{\sigma}^{\dagger}$, and the field amplitude in the k-th mode $\hat{a}_k$:

$$\frac{d\hat{\sigma}(t)}{dt} = -i\omega_\sigma\hat{\sigma} + i\sum_k \Omega_k \hat{D}\hat{a}_k \tag{8.10.8}$$

$$\frac{d\hat{D}}{dt} = 2i\sum_k \Omega_k \left(\hat{a}_k^\dagger \hat{\sigma} + \hat{\sigma}^\dagger \hat{a}_k\right) \tag{8.10.9}$$

$$\frac{d\hat{a}_k}{dt} = -i\omega_k \hat{a}_k - i\Omega_k \hat{\sigma} \tag{8.10.10}$$

Integration of Eq. (8.10.10) gives:

$$\hat{a}_k(t) = a_k(0)\exp(-i\omega_k t) - i\Omega_k \int_0^t d\tau \exp(-i\omega_k(t-\tau))\hat{\sigma}(\tau) \tag{8.10.11}$$

Substituting Eq. (8.10.11) in Eqs. (8.10.8) and (8.10.9), we arrive at the following system of equations:

$$\frac{d\hat{\sigma}(t)}{dt} = -i\omega_\sigma\hat{\sigma} + \hat{D}\sum_k |\Omega_k|^2 \int_0^t d\tau \exp(-i\omega_k(t-\tau))\hat{\sigma}(\tau) + i\hat{D}\sum_k \gamma_k \hat{a}_k(0)\exp(-i\omega_k t) \tag{8.10.12}$$

$$\begin{aligned}\frac{d\hat{D}}{dt} = &-2\sum_k |\Omega_k|^2 \int_0^t d\tau \left(\hat{\sigma}^\dagger(\tau)\hat{\sigma}(t)\exp(i\omega_k(t-\tau)) + \hat{\sigma}^\dagger(t)\hat{\sigma}(\tau)\exp(-i\omega_k(t-\tau))\right) \\ &+2i\sum_k \Omega_k \left(\hat{a}_k^\dagger(0)\hat{\sigma}(t)\exp(i\omega_k t) - \hat{\sigma}^\dagger(t)\hat{a}_k(0)\exp(-i\omega_k t)\right)\end{aligned} \tag{8.10.13}$$

Next, in Eqs. (8.10.12) and (8.10.13), we use the approximation of slowly varying amplitudes of the dipole moment:

$$\hat{\sigma}(t) \to \hat{\sigma}(t)\exp(-i\omega_\sigma t) \tag{8.10.14}$$

and change the variable $\tau \to t - \tau$. As a result, we obtain:

$$\frac{d\hat{\sigma}(t)}{dt} = \hat{D}\sum_k |\Omega_k|^2 \int_0^t d\tau \exp(i(\omega_\sigma - \omega_k)\tau)\hat{\sigma}(t-\tau) + i\hat{D}\sum_k \Omega_k \hat{a}_k(0)\exp(-i(\omega_k - \omega_\sigma)t) \tag{8.10.15}$$

The integrand in this equation oscillates rapidly; therefore, the main contribution to the integral comes from the time interval $\tau \leq 1/\omega_\sigma$. Since we consider times $t \gg 1/\omega_\sigma$, we can extend the upper limit of integration to ∞:

$$\frac{d\hat{D}}{dt} = -2\sum_k |\Omega_k|^2 \int_0^t d\tau \big[\hat{\sigma}^\dagger(t-\tau)\hat{\sigma}(t)\exp(-i(\omega_\sigma-\omega_k)\tau) + \hat{\sigma}^\dagger(t)\hat{\sigma}(t-\tau)\exp(i(\omega_\sigma-\omega_k)\tau)\big] + 2i\sum_k \Omega_k \big[\hat{a}_k^\dagger(0)\hat{\sigma}(t)\exp(i(\omega_k-\omega_\sigma)t) - \hat{\sigma}^\dagger(t)\hat{a}_k(0)\exp(-i(\omega_k-\omega_\sigma)t)\big]. \tag{8.10.16}$$

For a complete description of the TLS dynamics, we write an equation for the operator $\hat{\sigma}^\dagger(t)$, which is the Hermitian conjugation of Eq. (8.10.15):

$$\frac{d\hat{\sigma}^\dagger(t)}{dt} = \hat{D}\sum_k |\Omega_k|^2 \int_0^t d\tau \exp(-i(\omega_\sigma-\omega_k)\tau)\hat{\sigma}^\dagger(t-\tau) - i\hat{D}\sum_k \Omega_k \hat{a}_k^\dagger(0)\exp(i(\omega_k-\omega_\sigma)t) \tag{8.10.17}$$

For the sums on the right-hand sides of Eqs. (8.10.15)–(8.10.17), we introduce the notations:

$$\hat{F}_\sigma(t) = i\hat{D}(t)\sum_k \Omega_k \hat{a}_k(0)e^{i(\omega_\sigma-\omega_k)t} \tag{8.10.18}$$

$$\hat{F}_D(t) = 2i\sum_k \Omega_k \left(\hat{a}_k^\dagger(0)\hat{\sigma}(t)e^{-i(\omega_\sigma-\omega_k)t} - \hat{\sigma}^\dagger(t)\hat{a}_k(0)e^{i(\omega_\sigma-\omega_k)t}\right) \tag{8.10.19}$$

$$\hat{F}_{\sigma^\dagger}(t) = -i\sum_k \Omega_k \hat{a}_k^\dagger e^{-i(\omega_\sigma-\omega_k)t}\hat{D}(t) \tag{8.10.20}$$

Next, we use the Markov approximation, described in detail in Sect. 3.1. It means that we can neglect time non-locality in Eqs. (8.10.15) and (8.10.16) and change $\hat{\sigma}(t-\tau)$ to $\hat{\sigma}(t)$. Then, the upper limit of integration with respect to time is tended to ∞. Finally, we obtain:

$$\int_0^t d\tau\hat{\sigma}(t-\tau)\exp(\pm i(\omega-\omega_\sigma)\tau) \simeq \hat{\sigma}(t)\int_0^\infty d\tau\exp(\pm i(\omega-\omega_\sigma)\tau),$$
$$\int_0^t d\tau\hat{\sigma}^\dagger(t-\tau)\exp(\pm i(\omega-\omega_\sigma)\tau) \simeq \hat{\sigma}^\dagger(t)\int_0^\infty d\tau\exp(\pm i(\omega-\omega_\sigma)\tau) \tag{8.10.21}$$

As a result of the substitution of Eq. (8.10.21) into Eqs. (8.10.16) and (8.10.15), we obtain the following system of equations:

$$\frac{d\hat{\sigma}(t)}{dt} = \hat{D}(t)\hat{\sigma}(t)\sum_k |\Omega_k|^2 \int_0^\infty d\tau \exp(i(\omega_\sigma - \omega_k)\tau) + \hat{F}_\sigma(t) \tag{8.10.22}$$

$$\frac{d\hat{\sigma}^\dagger(t)}{dt} = \hat{\sigma}^\dagger(t)\hat{D}(t)\sum_k |\Omega_k|^2 \int_0^\infty d\tau \exp(i(\omega_\sigma - \omega_k)\tau) + \hat{F}_{\sigma^\dagger}(t) \tag{8.10.23}$$

$$\frac{d\hat{D}}{dt} = -2\hat{\sigma}^\dagger(t)\hat{\sigma}(t)\sum_k \left(\int_0^\infty d\tau \exp(i(\omega_\sigma - \omega_k)\tau) + \int_0^\infty d\tau \exp(-i(\omega_\sigma - \omega_k)\tau) \right) + \hat{F}_D(t) \tag{8.10.24}$$

where $\hat{F}_\sigma(t)$, $\hat{F}_{\sigma^\dagger}(t)$, $\hat{F}_D(t)$ are notations introduced in Eqs. (8.10.18)–(8.10.20).

To calculate the integrals, we employ the Sokhotski formula:

$$\int_0^\infty d\tau \exp(i(\omega_\sigma - \omega_k)\tau) = \pi\delta(\omega_\sigma - \omega_k) + i\mathrm{P}\frac{1}{\omega_\sigma - \omega_k} \tag{8.10.25}$$

Finally, we arrive at the following equations:

$$\frac{d\hat{\sigma}(t)}{dt} = -\left(\gamma_D^{(rad)}/2 + i\Delta\omega\right)\hat{\sigma}(t) + \hat{F}_\sigma(t) \tag{8.10.26}$$

$$\frac{d\hat{\sigma}^\dagger(t)}{dt} = -\left(\gamma_D^{(rad)}/2 - i\Delta\omega\right)\hat{\sigma}^\dagger(t) + \hat{F}_{\sigma^\dagger}(t) \tag{8.10.27}$$

$$\frac{d\hat{D}(t)}{dt} = -\gamma_D^{(rad)}\left(\hat{D} + \hat{I}\right) + \hat{F}_D(t) \tag{8.10.28}$$

where

$$\gamma_D^{(rad)}/2 = \pi\sum_k |\Omega(\omega_k)|^2\delta(\omega_k - \omega_\sigma) \tag{8.10.29}$$

This is the rate of spontaneous radiation that has been calculated in Problem 1.6.

Now, let us show now that the correlation properties of operators $\hat{F}_\sigma, \hat{F}_{\sigma^\dagger}, \hat{F}_D$ are similar to those for white noise. To do this, we need to compute the average of the simultaneous and two-time average values of the operators. We assume that the reservoir at all times is in the state of thermal equilibrium and its density matrix has the form:

$$\hat{\rho}_\mathrm{R}^\mathrm{th} = \exp\left(-\hat{H}_\mathrm{R}/kT\right)/\mathrm{Tr}\left(\exp\left(-\hat{H}_\mathrm{R}/kT\right)\right) \tag{8.10.32}$$

where operator $\hat{H}_\mathrm{R}$ is determined by the second term in Eq. (8.10.7).

Next, we need to obtain average values of the operators $\hat{a}_k$, $\hat{a}_k^\dagger$, $\hat{a}_k\hat{a}_{k'}$, $\hat{a}_k^\dagger\hat{a}_{k'}$, $\hat{a}_k\hat{a}_{k'}^\dagger$, $\hat{a}_k^\dagger\hat{a}_{k'}^\dagger$ that are determined by the density matrix as $\langle\hat{A}\rangle = \mathrm{Tr}\left(\hat{\rho}_{\mathrm{R}}^{\mathrm{th}}\hat{A}\right)$. We have:

$$\langle\hat{a}_k\rangle = 0, \left\langle\hat{a}_k^\dagger\right\rangle = 0, \left\langle\hat{a}_k^\dagger\hat{a}_{k'}\right\rangle = \overline{n}_k\delta_{kk'}, \left\langle\hat{a}_k^\dagger\hat{a}_{k'}\right\rangle = (1+\overline{n}_k)\delta_{kk'}, \tag{8.10.33}$$

here $\overline{n}_k = (\exp(\hbar\omega_k/kT) - 1)^{-1}$.

Using Eq. (8.10.33), we obtain:

$$\begin{aligned}\left\langle\hat{F}_\sigma(t)\hat{F}_\sigma(t')\right\rangle &= -\left\langle\hat{D}(t)\sum_k\Omega_k\hat{a}_k(0)e^{i(\omega_\sigma-\omega)t}\hat{D}(t')\sum_{k'}\Omega_{k'}\hat{a}_{k'}(0)e^{i(\omega_\sigma-\omega)t}\right\rangle \\ &= -\sum_{kk'}\hat{D}(t)\hat{D}(t')\Omega_k\Omega_{k'}e^{i(\omega_\sigma-\omega)t}e^{i(\omega_\sigma-\omega)t'}\langle\hat{a}_k(0)\hat{a}_{k'}(0)\rangle = 0\end{aligned} \tag{8.10.34}$$

and

$$\left\langle\hat{F}_{\sigma^\dagger}(t)\hat{F}_{\sigma^\dagger}(t')\right\rangle = 0 \tag{8.10.35}$$

Calculating the correlator $\left\langle\hat{F}_\sigma(t)\hat{F}_{\sigma^\dagger}(t')\right\rangle$ is not much harder:

$$\begin{aligned}\left\langle\hat{F}_\sigma(t)\hat{F}_{\sigma^\dagger}(t')\right\rangle &= \hat{D}(t)\hat{D}(t')\sum_{kk'}\Omega_k\Omega_{k'}^*\left\langle\hat{a}_k(0)\hat{a}_{k'}^\dagger(0)\right\rangle e^{i(\omega_\sigma-\omega_k)t}e^{-i(\omega_\sigma-\omega_{k'})t} \\ &= \hat{D}(t)\hat{D}(t')\sum_k|\Omega_k|^2(1+\overline{n}_k)e^{i(\omega_\sigma-\omega_k)(t-t')} \\ &= \hat{D}(t)\hat{D}(t')\int_0^\infty d\omega\rho(\omega)|\Omega(\omega)|^2(1+\overline{n}(\omega))\exp(i(\omega_\sigma-\omega)(t-t')) \\ &= \hat{D}(t)\hat{D}(t')\pi\rho(\omega_\sigma)|\Omega(\omega_\sigma)|^2(1+\overline{n}(\omega_\sigma))\delta(t-t') \\ &= \frac{\gamma_D^{(rad)}}{2}(\overline{n}(\omega)+1)\delta(t-t')\end{aligned} \tag{8.10.36}$$

In the last step, we used $\hat{D}(t)\hat{D}(t')\delta(t-t') = \hat{D}(t)\hat{D}(t)\delta(t-t') = \hat{1}\delta(t-t')$ and Eq. (8.10.29) for $\gamma_D^{(rad)}$.

In the same manner, we obtain:

$$\left\langle\hat{F}_{\sigma^\dagger}(t)\hat{F}_\sigma(t')\right\rangle = \frac{\gamma_D^{(rad)}}{2}\overline{n}(\omega_\sigma)\delta(t-t') \tag{8.10.37}$$

and

$$\begin{aligned}\left\langle \hat{F}_\sigma(t)\hat{F}_D(t')\right\rangle &= -2\hat{D}(t)\sum_{kk'}\Omega_k\Omega_{k'}\left\langle \hat{a}_k(0)\hat{a}^\dagger_{k'}(0)\right\rangle\hat{\sigma}(t')e^{i(\omega_\sigma-\omega_k)t}e^{-i(\omega_\sigma-\omega_k)t'}\\ &\quad +2\hat{D}(t)\sum_{kk'}\Omega_k\Omega_{k'}\langle \hat{a}_k(0)\hat{a}_{k'}(0)\rangle\hat{\sigma}^\dagger(t')e^{i(\omega_\sigma-\omega_k)t}e^{i(\omega_\sigma-\omega_k)t'}\\ &= -2\hat{D}(t)\hat{\sigma}(t')\sum_k|\Omega_k|^2(n_k+1)\hat{\sigma}(t')e^{i(\omega_\sigma-\omega_k)(t-t')}\\ &= -2\hat{D}(t)\hat{\sigma}(t')\int_0^\infty d\omega\rho(\omega)|\Omega(\omega)|^2(n(\omega)+1)e^{i(\omega_\sigma-\omega_k)(t-t')}\\ &= -2\hat{D}(t)\hat{\sigma}(t')\pi|\Omega(\omega_\sigma)|^2(n(\omega_\sigma)+1)\delta(t-t')\\ &= \gamma_D^{(rad)}\hat{\sigma}(t)(\overline{n}(\omega_\sigma)+1)\delta(t-t')\end{aligned} \tag{8.10.38}$$

In the last step, we used $\hat{D}(t)\hat{\sigma}(t')\delta(t-t')=\hat{D}(t)\hat{\sigma}(t)\delta(t-t')=-\hat{\sigma}(t)\delta(t-t')$.

Similarly, we obtain:

$$\left\langle \hat{F}_D(t)\hat{F}_\sigma(t')\right\rangle = -\gamma_D^{(rad)}\overline{n}(\omega)\hat{\sigma}(t)\delta(t-t') \tag{8.10.39}$$

$$\left\langle \hat{F}_{\sigma^\dagger}(t)\hat{F}_D(t')\right\rangle = -\gamma_D^{(rad)}\overline{n}(\omega)\hat{\sigma}^\dagger(t)\delta(t-t') \tag{8.10.40}$$

$$\left\langle \hat{F}_D(t)\hat{F}_{\sigma^\dagger}(t')\right\rangle = \gamma_D^{(rad)}(\overline{n}(\omega)+1)\hat{\sigma}^\dagger(t)\delta(t-t') \tag{8.10.41}$$

$$\begin{aligned}\left\langle \hat{F}_D(t)\hat{F}_D(t')\right\rangle &= -4\Bigg\langle\sum_k\Omega_k\left(a_k^\dagger(0)\hat{\sigma}(t)e^{-i(\omega_\sigma-\omega_k)t}-\hat{\sigma}^\dagger(t)a_k(0)e^{i(\omega_\sigma-\omega_k)t}\right)\\ &\quad\times\sum_{k'}\Omega_{k'}\left(a_{k'}^\dagger(0)\hat{\sigma}(t)e^{-i(\omega_\sigma-\omega_{k'})t}-\hat{\sigma}^\dagger(t)a_{k'}(0)e^{i(\omega_\sigma-\omega_{k'})t}\right)\Bigg\rangle\\ &= 4\sum_k|\Omega_k|^2\overline{n}_k\hat{\sigma}(t)\hat{\sigma}^\dagger(t')e^{-i(\omega_\sigma-\omega_k)(t-t')}\\ &\quad +4\sum_k|\Omega_k|^2(\overline{n}_k+1)\hat{\sigma}^\dagger(t)\hat{\sigma}(t')e^{i(\omega_\sigma-\omega_k)(t-t')}\\ &= 4\hat{\sigma}(t)\hat{\sigma}^\dagger(t')\int_0^\infty d\omega\rho(\omega)|\Omega(\omega)|^2n(\omega)e^{-i(\omega_\sigma-\omega)(t-t')}\\ &\quad +4\hat{\sigma}^\dagger(t)\hat{\sigma}(t')\int_0^\infty d\omega\rho(\omega)|\Omega(\omega)|^2(n(\omega)+1)e^{i(\omega_\sigma-\omega)(t-t')}\\ &= 4\hat{\sigma}(t)\hat{\sigma}^\dagger(t')\pi\rho(\omega_\sigma)|\Omega(\omega_\sigma)|^2n(\omega_\sigma)\delta(t-t')\\ &\quad +4\hat{\sigma}^\dagger(t)\hat{\sigma}(t')\pi\rho(\omega_\sigma)|\Omega(\omega_\sigma)|^2(n(\omega_\sigma)+1)\delta(t-t')\\ &= \gamma_D^{(rad)}\left(\overline{n}(\omega_\sigma)\left(1-\hat{D}(t)\right)+(\overline{n}(\omega_\sigma)+1)\left(1+\hat{D}(t)\right)\right)\delta(t-t')\end{aligned} \tag{8.10.42}$$

Here we have used the equalities:

$$\hat{\sigma}(t)\hat{\sigma}^{\dagger}(t')\delta(t-t') = \hat{\sigma}(t)\hat{\sigma}^{\dagger}(t)\delta(t-t') = \left(\hat{I} - \hat{D}(t)\right)\delta(t-t')/2$$

and

$$\hat{\sigma}^{\dagger}(t)\hat{\sigma}(t')\delta(t-t') = \hat{\sigma}^{\dagger}(t)\hat{\sigma}(t)\delta(t-t') = \left(\hat{I} + \hat{D}(t)\right)\delta(t-t')/2.$$

Combining expressions (8.10.34)–(8.10.42), we obtain the matrix of correlators (3.1.14) in Sect. 3.1:

$$M_{ij} = \gamma_D^{(rad)} \begin{pmatrix} \overline{n}(\omega_\sigma)/2 & 0 & -\overline{n}(\omega_\sigma)\hat{\sigma}^{\dagger}(t) \\ 0 & (\overline{n}(\omega_\sigma)+1)/2 & (\overline{n}(\omega_\sigma)+1)\hat{\sigma}(t) \\ -\overline{n}(\omega_\sigma)\hat{\sigma}(t) & (\overline{n}(\omega_\sigma)+1)\hat{\sigma}^{\dagger}(t) & \overline{n}(\omega_\sigma)\left(1-\hat{D}\right) + (\overline{n}(\omega_\sigma)+1)\left(1+\hat{D}\right) \end{pmatrix} \tag{8.10.43}$$

Problem 1.11
Derive correlation properties of the noise due to the TLS interaction with the dephasing reservoir.

Solution
The Hamiltonian of the TLS interacting with the dephasing reservoir has the form:

$$\hat{H} = \hbar\omega_\sigma \hat{\sigma}^{\dagger}\hat{\sigma} + \hbar\sum_m \omega_m \hat{b}^{\dagger}\hat{b} + \hbar\sum_m \gamma_m \left(\hat{b}_m^{\dagger}\hat{\sigma}^{\dagger}\hat{\sigma} + \hat{\sigma}^{\dagger}\hat{\sigma}\hat{b}_m\right) \tag{8.11.1}$$

The last term in this Hamiltonian has the form of the Fröhlich Hamiltonian, which describes the TLS interaction with the set of phonon modes (see discussion in Part II). Heisenberg equations of motion for the operators $\hat{\sigma}$, $\hat{\sigma}^{\dagger}\hat{\sigma}$, and $\hat{b}_m$ have the form:

$$\frac{d\hat{\sigma}}{dt} = -i\omega_\sigma\hat{\sigma} - i\sum_m \gamma_m\left(\hat{b}_m^{\dagger}\hat{\sigma} + \hat{\sigma}\hat{b}_m\right) \tag{8.11.2}$$

$$\frac{d\hat{\sigma}^{\dagger}\hat{\sigma}}{dt} = 0 \tag{8.11.3}$$

$$\frac{d\hat{b}_m}{dt} = -i\omega_m\hat{b}_m - i\gamma_m\hat{\sigma}^{\dagger}\hat{\sigma} \tag{8.11.4}$$

The solution of Eq. (8.11.4) can be written as

$$\hat{b}_m(t) = \hat{b}(0)\exp(-i\omega_m t) - i\gamma_m\int_0^t d\tau \exp(-i\omega_m(t-\tau))\hat{\sigma}^{\dagger}(\tau)\hat{\sigma}(\tau) \tag{8.11.5}$$

According to Eq. (8.11.3), $\hat{\sigma}^\dagger\hat{\sigma}$ does not depend on time, so that $\hat{\sigma}^\dagger(\tau)\hat{\sigma}(\tau) = \hat{\sigma}^\dagger(t)\hat{\sigma}(t) = \hat{\sigma}^\dagger\hat{\sigma}$; thus, while calculating the integral, $\hat{\sigma}^\dagger\hat{\sigma}$ can be factored out. After that, we substitute Eq. (8.11.5) into Eq. (8.11.2) to obtain:

$$\begin{aligned}\frac{d\hat{\sigma}}{dt} &= -i\omega_\sigma\hat{\sigma} - i\sum_m \gamma_m\left(\hat{b}_m^\dagger(0)\hat{\sigma}\exp(i\omega_m t) + \hat{\sigma}\hat{b}(0)\exp(-i\omega_m t)\right) - \\ &\quad - i\sum_m\left(\gamma_m i\gamma_m\hat{\sigma}^\dagger\hat{\sigma}\hat{\sigma}\int_0^t d\tau\exp(i\omega_m\tau) + \gamma_m\hat{\sigma}(-i\gamma_m)\hat{\sigma}^\dagger\hat{\sigma}\int_0^t d\tau\exp(-i\omega_m\tau)\right) \\ &= \left(-i\omega_\sigma - \sum_m\gamma_m^2\int_0^t d\tau\exp(-i\omega_m\tau)\right)\hat{\sigma} + \hat{F}_\sigma(t)\end{aligned} \tag{8.11.6}$$

where, at the last step, we use $\hat{\sigma}^\dagger\hat{\sigma}\hat{\sigma} = 0$ and $\hat{\sigma}\hat{\sigma}^\dagger\hat{\sigma} = \hat{\sigma}$ (see Problem 1.1) and introduce the notation

$$F_\sigma(t) = -i\sum_m\gamma_m\left(\hat{b}_m^\dagger(0)\hat{\sigma}\exp(i\omega_m t) + \hat{\sigma}\hat{b}(0)\exp(-i\omega_m t)\right) \tag{8.11.7}$$

Further, to apply the Markovian approximation, we turn to the new variable $\widehat{\widehat{\sigma}} = \hat{\sigma}\exp(i\omega_\sigma\tau)$. Using Eq. (8.11.6) for $\hat{\sigma}$, we can obtain Heisenberg equation for the operator $\widehat{\widehat{\sigma}}$ which has the form:

$$\frac{d\widehat{\widehat{\sigma}}}{dt} = -\sum_m\gamma_m^2\int_0^t d\tau\exp(i\omega_m(t-\tau))\widehat{\widehat{\sigma}} + \hat{F}_\sigma(t)e^{i\omega_\sigma t} \tag{8.11.8}$$

The first term on the right-hand side can be approximately evaluated with the help of the Markov approximation. Namely, the function $\exp(i\omega_m(t-\tau))$ is fast oscillating except for the point in the vicinity of the upper limit of the integral, $\tau = t$. Thus, only the neighborhood of this point makes a significant contribution to the integral. For this reason, we can expand the lower limit to negative infinity:

$$\begin{aligned}&-\sum_m\gamma_m^2\int_{-\infty}^t d\tau\exp(i\omega_m(t-\tau)) = -\sum_m\gamma_m^2\int_0^\infty d\tau\exp(i\omega_m\tau) \\ &= -\sum_m\gamma_m^2\left(\pi\delta(\omega_m) - iP\left(\frac{1}{\omega_m}\right)\right) = -\int_0^\infty d\omega\Pi_\sigma(\omega)\gamma^2(\omega)\left(\pi\delta(\omega_m) - iP\left(\frac{1}{\omega_m}\right)\right) \\ &= i\Delta\omega_\sigma - \gamma_\sigma\end{aligned} \tag{8.11.9}$$

where we use the density of dephasing reservoir state $\Pi_{deph}(\omega)$ to transition from summation to integration and, at the last step, introduce the notation:

$$\gamma_\sigma = \pi\Pi(0)\gamma^2(0), \qquad \Delta\omega_\sigma = P\int d\omega \frac{\gamma^2(\omega)}{\omega} \tag{8.11.10}$$

Using this notation and returning to the primary variable $\hat{\sigma}$, from Eq. (8.11.8), we obtain the following equation:

$$\frac{d\hat{\sigma}}{dt} = (-i(\omega_\sigma + \Delta\omega_\sigma) - \gamma_\sigma)\hat{\sigma} + \hat{F}_\sigma(t) \tag{8.11.11}$$

Let us show that the function $\hat{F}_\sigma(t)$ has the properties of random noise. For this purpose, we calculate the correlator $\left\langle \hat{F}_\sigma^\dagger(t+\tau)\hat{F}_\sigma(t)\right\rangle$:

$$\begin{aligned}
&\left\langle \hat{F}_\sigma^\dagger(t+\tau)\hat{F}_\sigma(t)\right\rangle \\
&= \sum_{m_1,m_2} \gamma_{m1}\gamma_{m2}\left(\hat{b}_{m1}\hat{\sigma}^\dagger \exp(-i\omega_{m1}(t+\tau)) + \hat{\sigma}^\dagger\hat{b}_{m1}^\dagger \exp(i\omega_{m1}(t+\tau))\right) \\
&\quad \times \left(\hat{b}_{m2}^\dagger\hat{\sigma}\exp(i\omega_{m2}t) + \hat{\sigma}\hat{b}_{m2}\exp(-i\omega_{m2}t)\right) \\
&= \hat{\sigma}^\dagger\hat{\sigma}\sum_{m_1,m_2}\gamma_{m1}\gamma_{m2}\left(\left(\hat{b}_{m1}e^{-i\omega_{m1}(t+\tau)} + \hat{b}_{m1}^\dagger e^{i\omega_{m1}(t+\tau)}\right)\left(\hat{b}_{m2}^\dagger e^{i\omega_{m2}t} + \hat{b}_{m2}e^{-i\omega_{m2}t}\right)\right)
\end{aligned} \tag{8.11.12}$$

Supposing that the dephasing reservoir is in thermal equilibrium, we can use the following equalities: $\left\langle \hat{b}_{m1}^\dagger\hat{b}_{m2}\right\rangle = \delta_{m1,m2}\overline{n}_{m1}$, $\left\langle \hat{b}_{m1}\hat{b}_{m2}^\dagger\right\rangle = \delta_{m1,m2}(\overline{n}_{m1}+1)$, $\left\langle \hat{b}_{m1}\hat{b}_{m2}\right\rangle = \left\langle \hat{b}_{m1}^\dagger\hat{b}_{m2}^\dagger\right\rangle = 0$. Then, Eq. (8.11.12) is transformed to

$$\begin{aligned}
&\left\langle \hat{F}_\sigma^\dagger(t+\tau)\hat{F}_\sigma(t)\right\rangle = \hat{\sigma}^\dagger\hat{\sigma}\sum_m \gamma_m^2((n_m+1)\exp(-i\omega_m\tau) + n_m\exp(i\omega_m\tau)) = \\
&= \hat{\sigma}^\dagger\hat{\sigma}\int_0^\infty d\omega\Pi(\omega)\gamma^2(\omega)((\overline{n}(\omega)+1)\exp(-i\omega\tau) + \overline{n}(\omega)\exp(i\omega\tau)) \\
&\simeq \hat{\sigma}^\dagger\hat{\sigma}\pi\Pi(0)\gamma^2(0)(2\overline{n}_\sigma(0)+1)\delta(\tau) = \hat{\sigma}^\dagger\hat{\sigma}\gamma_\sigma(2\overline{n}_\sigma(0)+1)\delta(\tau)
\end{aligned} \tag{8.11.13}$$

Similarly, we obtain:

$$\left\langle \hat{F}_\sigma(t+\tau)\hat{F}_\sigma^\dagger(t)\right\rangle \simeq \hat{\sigma}\hat{\sigma}^\dagger\gamma_\sigma(2\overline{n}_\sigma(0)+1)\delta(\tau) \tag{8.11.14}$$

Other correlators are zero:

$$\left\langle \hat{F}_\sigma(t+\tau)\hat{F}_\sigma(t)\right\rangle = \left\langle \hat{F}_\sigma^\dagger(t+\tau)\hat{F}_\sigma^\dagger(t)\right\rangle = 0, \quad \left\langle \hat{F}_\sigma(t)\right\rangle = \left\langle \hat{F}_\sigma^\dagger\right\rangle = 0 \qquad (8.11.15)$$

Thus, the correlation matrix for the dephasing reservoir has the form:

$$M_{deph} = \gamma_\sigma \begin{pmatrix} 0 & \hat{\sigma}\hat{\sigma}^\dagger\gamma_\sigma(2\overline{n}_\sigma(0)+1) & 0 \\ \hat{\sigma}^\dagger\hat{\sigma}\gamma_\sigma(2\overline{n}_\sigma(0)+1) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (8.11.16)$$

Problem 1.12
Prove the quantum regression theorem.

Theorem Let us consider the time-dependent column vector of operators $\hat{\mathbf{X}}=\{\hat{X}_1, \hat{X}_2, \ldots, \hat{X}_n\}$ whose dynamics is governed by the closed linear system of differential equations with Markovian noise operators on the right-hand sides (this is a key requirement because the assertion of the theorem is obvious for a zero right-hand side, but false for an arbitrary one):

$$\frac{d}{dt}\hat{\mathbf{X}} = \mathbf{M}\cdot\widehat{\mathbf{X}} + \hat{\mathbf{F}}(t),$$

where $\mathbf{M}$ is a time-independent complex-valued matrix and $\hat{\mathbf{F}}(t) = \left\{\hat{F}_1(t), \hat{F}_2(t), , \ldots, \hat{F}_n(t)\right\}$ is the column vector of noise operators with the following properties:

$$\left\langle \hat{\mathbf{F}}(t)\right\rangle = 0, \quad \left\langle \hat{\mathbf{F}}(t_1)\hat{\mathbf{F}}^T(t_2)\right\rangle = 2\mathbf{D}\delta(t_1-t_2)$$

where $\mathbf{D}$ is the so-called diffusion matrix.

The quantum regression theorem states that the expected values of two-time correlators

$$\left\langle \hat{\mathbf{X}}(t+\tau)\hat{\mathbf{X}}^T(t)\right\rangle = \begin{pmatrix} \left\langle \hat{X}_1(t+\tau)\hat{X}_1(t)\right\rangle & \cdots & \left\langle \hat{X}_1(t+\tau)\hat{X}_n(t)\right\rangle \\ \vdots & \ddots & \vdots \\ \left\langle \hat{X}_n(t+\tau)\hat{X}_1(t)\right\rangle & \cdots & \left\langle \hat{X}_n(t+\tau)\hat{X}_n(t)\right\rangle \end{pmatrix}$$

satisfy the system of equations:

$$\frac{d}{d\tau}\left\langle \hat{\mathbf{X}}(t+\tau)\hat{\mathbf{X}}^T(t)\right\rangle = \mathbf{M}\left\langle \hat{\mathbf{X}}(t+\tau)\hat{\mathbf{X}}^T(t)\right\rangle$$

with the same complex-valued matrix $\mathbf{M}$ that describes the dynamics of the column vector of operators $\hat{\mathbf{X}}$.

The Proof

First, we write the solution to the system of equations for $\hat{\mathbf{X}}(t)$ in the form:

$$\hat{\mathbf{X}}(t) = \exp(\mathbf{M}t)\hat{\mathbf{X}}(0) + \int_0^t d\tau' \exp(\mathbf{M}(t-\tau'))\hat{\mathbf{F}}(\tau')$$

or

$$\hat{\mathbf{X}}(t+\tau) = \exp((t+\tau)\mathbf{M})\hat{\mathbf{X}}(0) + \int_0^{t+\tau} d\tau' \exp((t+\tau-\tau')\mathbf{M})\hat{\mathbf{F}}(\tau')$$

The transposition of this expression gives the equation for the corresponding row vector:

$$\hat{\mathbf{X}}^T(t) = \hat{\mathbf{X}}^T(0)\exp\left(t\mathbf{M}^T\right) + \int_0^t d\tau''\hat{\mathbf{F}}^T(\tau'')\exp\left((t-\tau'')\mathbf{M}^T\right)$$

Multiplying these expressions and averaging over the noise, we obtain:

$$\begin{aligned}\left\langle \hat{\mathbf{X}}(t+\tau)\hat{\mathbf{X}}^T(t)\right\rangle &= \exp((t+\tau)\mathbf{M})\left\langle \hat{\mathbf{X}}(0)\hat{\mathbf{X}}^T(0)\right\rangle \exp\left(t\mathbf{M}^T\right) \\ &+ \int_0^{t+\tau} d\tau' \int_0^t d\tau'' \exp((t+\tau-\tau')\mathbf{M})\left\langle \hat{\mathbf{F}}(\tau')\hat{\mathbf{F}}^T(\tau'')\right\rangle \exp\left((t-\tau'')\mathbf{M}^T\right)\end{aligned}$$

where we use that $\left\langle \hat{\mathbf{F}}(t)\right\rangle = 0$. The differentiation of this equation over τ gives:

$$\begin{aligned}\frac{d}{d\tau}\left\langle \hat{\mathbf{X}}(t+\tau)\hat{\mathbf{X}}^T(t)\right\rangle &= \mathbf{M}\exp((t+\tau)\mathbf{M})\left\langle \hat{\mathbf{X}}(0)\hat{\mathbf{X}}^T(0)\right\rangle \exp\left(t\mathbf{M}^T\right) \\ &+ \mathbf{M}\int_0^{t+\tau} d\tau' \int_0^t d\tau'' \exp((t+\tau-\tau')\mathbf{M})\left\langle \hat{\mathbf{F}}(\tau')\hat{\mathbf{F}}^T(\tau'')\right\rangle \exp\left((t-\tau'')\mathbf{M}^T\right) \\ &+ \int_0^t d\tau''\left\langle \hat{\mathbf{F}}(t+\tau)\hat{\mathbf{F}}^T(\tau'')\right\rangle \exp\left((t-\tau'')\mathbf{M}^T\right)\end{aligned}$$

The last term in this equation is zero because

$$\int_0^t d\tau''\left\langle \hat{\mathbf{F}}(t+\tau)\hat{\mathbf{F}}^T(\tau'')\right\rangle \exp\left(\mathbf{M}^T(t-\tau'')\right) = 2\mathbf{D}\int_0^t d\tau''\delta(t+\tau-\tau'')\exp\left(\mathbf{M}^T(t-\tau'')\right) = 0$$

The integral is equal to zero because for $\tau > 0$, the δ-function is zero inside the integration interval. Finally, we obtain:

$$\frac{d}{d\tau}\left\langle \hat{\mathbf{X}}(t+\tau)\hat{\mathbf{X}}^T(t)\right\rangle = M\exp(M(t+\tau))\left\langle \hat{\mathbf{X}}(0)\hat{\mathbf{X}}^T(0)\right\rangle \exp\left(M^T t\right)$$
$$+M\int_0^{t+\tau} d\tau' \int_0^t d\tau'' \exp(M(t+\tau-\tau'))\left\langle \hat{\mathbf{F}}(\tau')\hat{\mathbf{F}}^T(\tau'')\right\rangle \exp\left(M^T(t-\tau'')\right)$$
$$= M\left\langle \hat{\mathbf{X}}(t+\tau)\hat{\mathbf{X}}^T(t)\right\rangle$$

which proves the regression theorem.

Problem 1.13
Derive initial condition (3.4.36)–(3.4.38) for the system (3.4.35):

$$\left\langle \Delta\hat{\sigma}^\dagger(t_{st})\Delta\hat{\sigma}(t_{st})\right\rangle_{\tau=0} = \left(1+\left\langle \hat{D}\right\rangle_{st}\right)/2 - \left\langle \hat{\sigma}^\dagger\right\rangle_{st}\left\langle \hat{\sigma}\right\rangle_{st}$$
$$\left\langle \Delta\hat{\sigma}^\dagger(t_{st})\Delta\hat{\sigma}^\dagger(t_{st})\right\rangle = -\left\langle \hat{\sigma}^\dagger\right\rangle_{st}^2 \tag{8.13.1}$$
$$\left\langle \Delta\hat{\sigma}^\dagger(t_{st})\Delta\hat{D}(t_{st})\right\rangle = -\left\langle \hat{\sigma}^\dagger\right\rangle_{st}\left(1+\left\langle \hat{D}\right\rangle_{st}\right)$$

Solution
To derive Eqs. (3.4.36)–(3.4.38), we use the definition of $\Delta\sigma = \hat{\sigma} - \langle\hat{\sigma}\rangle\hat{I}$, $\Delta\hat{\sigma}^\dagger = \hat{\sigma}^\dagger - \left\langle\hat{\sigma}^\dagger\right\rangle\hat{I}$, and $\Delta\hat{D} = \hat{D} - \left\langle\hat{D}\right\rangle\hat{I}$. Further, we use the rules of multiplications of the operators $\hat{\sigma}$, $\hat{\sigma}^\dagger$, $\hat{D}$ (Eq. (8.13.1)) to obtain

$$\begin{aligned}\left\langle \Delta\hat{\sigma}^\dagger\Delta\hat{\sigma}\right\rangle &= \left\langle \left(\hat{\sigma}^\dagger - \left\langle\hat{\sigma}^\dagger\right\rangle\hat{I}\right)\left(\hat{\sigma} - \langle\hat{\sigma}\rangle\hat{I}\right)\right\rangle \\ &= \left\langle \hat{\sigma}^\dagger\hat{\sigma} - \hat{\sigma}^\dagger\langle\hat{\sigma}\rangle - \hat{\sigma}\left\langle\hat{\sigma}^\dagger\right\rangle + \left\langle\hat{\sigma}^\dagger\right\rangle\langle\hat{\sigma}\rangle\right\rangle \\ &= \left(1+\left\langle\hat{D}\right\rangle\right)/2 - \left\langle\hat{\sigma}^\dagger\right\rangle\langle\hat{\sigma}\rangle - \left\langle\hat{\sigma}^\dagger\right\rangle\langle\hat{\sigma}\rangle + \left\langle\hat{\sigma}^\dagger\right\rangle\langle\hat{\sigma}\rangle \\ &= \left(1+\left\langle\hat{D}\right\rangle\right)/2 - \left\langle\hat{\sigma}^\dagger\right\rangle\langle\hat{\sigma}\rangle\end{aligned} \tag{8.13.2}$$

In the latter equation, we use the equality $\hat{\sigma}^\dagger\hat{\sigma} = \left(1+\hat{D}\right)/2$. Further, in the last line of Eq. (8.13.2), one needs to substitute $\left\langle\hat{D}\right\rangle$, $\left\langle\hat{\sigma}^\dagger\right\rangle$, and $\langle\hat{\sigma}\rangle$, by the stationary values determined by Eq. (3.4.32) from the main text. After algebraic transformation, we arrive at Eq. (3.4.36). Similarly, one can obtain Eqs. (3.4.37) and (3.4.38).

Problem 1.14
Show that the operator $\hat{D}(z) = \exp\left(z\hat{a}^\dagger - z^*\hat{a}\right)$ shifts the quadrature operators $\hat{Q} = \sqrt{\hbar/(2\omega)}\left(\hat{a}+\hat{a}^\dagger\right)$ and $\hat{P} = -i\sqrt{\hbar\omega/2}\left(\hat{a}-\hat{a}^\dagger\right)$, namely,

$$\hat{D}(p_0,q_0)\hat{Q}\hat{D}^{-1}(p_0,q_0) = \hat{Q} - q_0\hat{1} \tag{8.14.1}$$
$$\hat{D}(p_0,q_0)\hat{P}\hat{D}^{-1}(p_0,q_0) = \hat{P} - p_0\hat{1} \tag{8.14.2}$$

Solution

The operator $\hat{D}(z) = \exp\left(z\hat{a}^{\dagger} - z^{*}\hat{a}\right)$ can be presented in the following equivalent forms:

$$\hat{D}(z) = \exp\left[\left(\hat{a}^{\dagger} - \hat{a}\right)\mathrm{Re}\, z + i\left(\hat{a}^{\dagger} + \hat{a}\right)\mathrm{Im} z\right] = \exp\left[i\left(p_0\hat{Q} - q_0\hat{P}\right)/\hbar\right] = \hat{D}(q_0, p_0) \tag{8.14.3}$$

where $q_0 = \sqrt{2\hbar/\omega}\,\mathrm{Re}\, z$ and $p_0 = \sqrt{2\hbar\omega}\mathrm{Im} z$.

To prove the validity of Eq. (8.14.1), it is convenient to employing the Lie product formula:

$$e^{\xi Y} X e^{-\xi Y} = X + \xi[Y, X] + \frac{\xi^2}{2}[Y, [Y, X]] + \ldots \tag{8.14.4}$$

Using notations $\hat{D}(z) = \exp\left[i\left(p_0\hat{Q} - q_0\hat{P}\right)/\hbar\right] = \exp\left[\hat{Y}\right]$, where $\hat{Y} = (i/\hbar)\left(p_0\hat{Q} - q_0\hat{P}\right)$, $\xi = 1$, and $\hat{X} = \hat{Q}$, the left-hand side of Eq. (8.14.4) becomes $e^{Y}\hat{Q}e^{-Y}$; then, employing the Lie product formula, we obtain:

$$e^{Y}\hat{Q}e^{-Y} = \hat{Q} + \left[Y, \hat{Q}\right] + \left[\hat{Y}, \left[\widehat{\hat{Y}, Q}\right]\right] + \ldots. \tag{8.14.5}$$

Thus, we should calculate the commutators $\left[\hat{Y}, \hat{Q}\right]$, $\left[\hat{Y}, \left[\widehat{\hat{Y}, Q}\right]\right]$, and so on.

Taking into account that $\left[\hat{Q}, \hat{P}\right] = i\hbar$, we can obtain:

$$\begin{aligned}\left[\hat{Y}, \hat{Q}\right] &= \left[(i/\hbar)\left(p_0\hat{Q} - q_0\hat{P}\right), Q\right] \\ &= (i/\hbar)\left\{\left(p_0\hat{Q} - q_0\hat{P}\right)\hat{Q} - \hat{Q}\left(p_0\hat{Q} - q_0\hat{P}\right)\right\} \\ &= (i/\hbar)\left\{p_0\hat{Q}^2 - q_0\hat{P}\hat{Q} - p_0\hat{Q}^2 + q_0\hat{Q}\hat{P}\right\} = (iq_0/\hbar)\left[\hat{Q}, \hat{P}\right] = -q_0\hat{1}\end{aligned} \tag{8.14.6}$$

$\left[\hat{Y}, \left[\widehat{\hat{Y}, Q}\right]\right] \sim \left[\hat{Y}, \hat{1}\right] = 0$. Consequently, all other commutators are equal to zero as well.

Finally, we arrive at Eq. (8.14.1).

The equality (8.14.2) is obtained using $\hat{X} = \hat{P}$.

Problem 1.15

Prove that $\langle z|\hat{Q}|z\rangle = q_0$ and $\langle z|\hat{P}|z\rangle = p_0$.

Solution

These equations are the consequences of the result of Problem 1.14:

$$\langle z|\hat{Q}|z\rangle = \langle 0|\hat{D}^{\dagger}(z)\hat{Q}\hat{D}^{\dagger}(z)|0\rangle = \langle 0|\hat{Q} + q_0\hat{1}|0\rangle = q_0 \tag{8.15.1}$$

and

$$\langle z|\hat{P}|z\rangle = \hat{D}(q_0,p_0)\hat{P}\hat{D}^{-1}(q_0,p_0) = p_0. \tag{8.15.2}$$

Problem 1.16
Prove that $|z\rangle = \hat{D}(z)|0\rangle$ is the eigenvector of the annihilation operator $\hat{a}$, where $\hat{D}(z) = \exp\left(z\hat{a}^\dagger - z^*\hat{a}\right)$ and $\hat{a}|z\rangle = z|z\rangle$.

Solution
One can check the validity of the following identities:

$$\begin{aligned} 0 &= {}_{\hat{a}|0\rangle = 0}\hat{D}(z)\hat{a}|0\rangle = {}_{|0\rangle = \hat{D}^{-1}(z)|z\rangle}\hat{D}(z)\hat{a}\hat{D}^{-1}(z)|z\rangle \\ &= {}_{\hat{D}(z) = \exp\left[\left(z\hat{a}^\dagger - z^*\hat{a}\right)\right]}\exp\left(z\hat{a}^\dagger - z^*\hat{a}\right)\hat{a}\exp\left(z^*\hat{a} - z\hat{a}^\dagger\right)|z\rangle \end{aligned} \tag{8.16.1}$$

Using the Lie product formula, Eq. (8.14.4)

$$e^{\xi Y}Xe^{-\xi Y} = X + \xi[Y,X] + \frac{\xi^2}{2}[Y,[Y,X]] + \ldots,$$

for $\xi = 1$, $\hat{Y} = \left(z\hat{a}^\dagger - z^*\hat{a}\right)$, $\hat{X} = \hat{a}$, and $\hat{D}(z) = \exp\left[\hat{Y}\right]$, we arrive at the following equation:

$$0 = \exp\left(\hat{Y}\right)\hat{a}\exp\left(-\hat{Y}\right)|z\rangle = \left(\hat{a} + [Y,\hat{a}] + \left[\hat{Y},\left[\hat{Y},\hat{a}\right]\right] + \ldots\right)|z\rangle. \tag{8.16.2}$$

We can see that

$$\begin{aligned} \left[\hat{Y},a\right] &= \left(z\hat{a}^\dagger - z^*\hat{a}\right)\hat{a} - \hat{a}\left(z\hat{a}^\dagger - z^*\hat{a}\right) = z\hat{a}^\dagger\hat{a} - z^*\hat{a}\hat{a} - z\hat{a}\hat{a}^\dagger + z^*\hat{a}\hat{a} \\ &= -z\left[\hat{a},\hat{a}^\dagger\right] = -z\hat{1} \end{aligned} \tag{8.16.3}$$

and $\left[\hat{Y},\left[\hat{\hat{Y}},Q\right]\right] \sim \left[\hat{Y},\hat{1}\right] = 0$. Consequently, all other commutators are also equal to zero. Finally, we arrive at the equation:

$$\left(\hat{a} + [Y,\hat{a}] + \left[\hat{Y},\left[\hat{Y},\hat{a}\right]\right]\right)|z\rangle = \left(\hat{a} - z\hat{1}\right)|z\rangle = 0 \text{ or } \hat{a}|z\rangle = z|z\rangle. \tag{8.16.4}$$

Problem 1.17
Show the following expansion:

$$|z\rangle = \exp\left(-\frac{1}{2}|z|^2\right)\sum\frac{z^n}{\sqrt{n!}}|n\rangle. \tag{8.17.1}$$

Solution
The coherent state can be expanded over the basis of the Fock states $\{|m\rangle\}$. For operators $\hat{A}$ and $\hat{B}$, which commutator is proportional to the identity operator we can employ Weil enequality $\exp\left(\hat{A}+\hat{B}\right) = \exp\left(\hat{A}\right)\exp\left(\hat{B}\right)\exp\left(-\left[\hat{A},\hat{B}\right]/2\right)$ to obtain:

$$\hat{D}(z) = \exp\left(z\hat{a}^\dagger - z^*\hat{a}\right) = \exp\left(-\frac{1}{2}zz^*\left[\hat{a}^\dagger, \hat{a}\right]\right)\exp\left(z\hat{a}^\dagger\right)\exp\left(-z^*\hat{a}\right) \tag{8.17.2}$$

Using Eq. (8.17.2), we arrive at

$$\begin{aligned}|z\rangle = \hat{D}(z)|0\rangle = e^{\left(-\frac{1}{2}zz^*\right)}e^{\left(z\hat{a}^\dagger\right)}e^{\left(-z^*\hat{a}\right)}|0\rangle \underset{\hat{a}|0\rangle=0}{=} e^{\left(-\frac{1}{2}zz^*\right)}e^{\left(z\hat{a}^\dagger\right)}|0\rangle \\ = e^{\left(-\frac{1}{2}|z|^2\right)}\sum\frac{z^n}{n!}\left(\hat{a}^\dagger\right)^n|0\rangle \underset{|n\rangle=(n!)^{-1/2}\left(\hat{a}^\dagger\right)^n|0\rangle}{=} \exp\left(\frac{1}{2}|z|^2\right)\sum\frac{z^n}{\sqrt{n!}}|n\rangle.\end{aligned} \tag{8.17.3}$$

where we have used the formula from Problem 1.6: $|n\rangle = \left(\hat{a}^\dagger\right)^n|0\rangle = (n!)^{-1/2}\left(\hat{a}^\dagger\right)^n|0\rangle$.

From Eq. (8.17.3), it follows that $|z\rangle$ is neither the eigenfunction of the operator of the number of quanta, $\hat{n} = \hat{a}^\dagger\hat{a}$, nor of the energy operator $\hat{H} = \hbar\omega_a\hat{a}^\dagger\hat{a}$.

Problem 1.18
Prove the completeness of the basis of the coherent states, i.e., the following identity:

$$\begin{gathered}\pi^{-1}\int|z\rangle\langle z|dz = \hat{I}, \\ \langle z|z'\rangle = \exp\left(-|z-z'|^2/2\right) \neq 0, \\ |\psi\rangle = \hat{I}|z\rangle = \pi^{-1}\int|z'\rangle\langle z'|\psi\rangle dz'\end{gathered} \tag{8.18.1}$$

Solution
To prove the statements, we use the expansion of the coherent state into Fock states (Problem 1.17) $|z\rangle = \exp\left(\frac{1}{2}|z|^2\right)\sum\frac{z^n}{\sqrt{n!}}|n\rangle$:

$$\begin{aligned}\int|z\rangle\langle z|d^2z &= \int\exp\left(-|z|^2\right)\sum_{n,m}|n\rangle\langle m|\frac{z^n(z^*)^m}{(n!m!)^{1/2}}d^2z \\ &\underset{z=r\exp(i\varphi)}{=} \int_0^\infty e^{-r^2}\sum_{n,m}|n\rangle\langle m|\frac{r^{n+m}}{(n!m!)^{1/2}}rdr\int_0^{2\pi}e^{i(n-m)\varphi}d\varphi \\ &= 2\pi\sum_{n,m}|n\rangle\langle n|\int_0^\infty e^{-r^2}\frac{r^{2n+1}}{n!}dr \\ &\int_0^{2\pi}e^{i(n-m)\varphi}d\varphi = 2\pi\delta_{n,m} \\ &= \pi\hat{1} \\ &\int_0^\infty e^{-r^2}r^{2n+1}dr = n!/2\end{aligned} \tag{8.18.2}$$

The coherent states are non-orthogonal:

$$\begin{aligned}\langle z|z'\rangle &= \exp\Big(-\Big(|z|^2+|z'|^2\Big)/2\Big)\sum_{n,m}\langle n|m\rangle\frac{(z^*)^n(z')^m}{(n!m!)^{1/2}}\\ &= \exp\Big(-\Big(|z|^2+|z'|^2\Big)/2+z^*z'\Big)=\exp\Big(-|z-z'|^2/2\Big)\neq 0\end{aligned} \tag{8.18.3}$$

Due to the completeness of the basis of coherent states, any other state can be expanded over this basis:

$$|\psi\rangle=\hat{1}|z\rangle=\pi^{-1}\int|z'\rangle\langle z'|\psi\rangle dz' \tag{8.18.4}$$

Problem 1.19
Find the expansion of the operator $\hat{\sigma}$ in terms of the eigenfunctions of the Jaynes-Cummings Hamiltonian:

$$\begin{aligned}&|+,n\rangle=\cos\varphi_n|e,n-1\rangle+\sin\varphi_n|g,n\rangle,\\ &|-,n\rangle=-\sin\varphi_n|e,n-1\rangle+\cos\varphi_n|g,n\rangle,\\ &\langle-,n|=-\sin\varphi_n\langle e,n-1|+\cos\varphi_n\langle g,n|,\\ &\langle+,n|=\cos\varphi_n\langle e,n-1|+\sin\varphi_n\langle g,n|,\qquad n=1,2,\ldots;\end{aligned} \tag{8.19.1}$$

with $\tan(2\varphi_n)=2\Omega_R\sqrt{n}/|\Delta|$ (see (2.2.4)).

Namely, we need to find

$$\langle+,n|\hat{\sigma}|+,n\rangle,\langle+,n|\hat{\sigma}|-,n\rangle,\langle-,n|\hat{\sigma}|+,n\rangle,\langle-,n|\hat{\sigma}|-,n\rangle.$$

Solution
Since the Jaynes-Cummings Hamiltonian is Hermitian, its eigenstates form a complete basis, and the "factorization of unity" is valid:

$$\hat{I}=|g,0\rangle\langle g,0|+\sum_{n=1}^{\infty}|-,n\rangle\langle-,n|+\sum_{n=1}^{\infty}|+,n\rangle\langle+,n| \tag{8.19.2}$$

Using Eq. (8.19.2) we should consider the explicit expression for the operator $\hat{\sigma}=\hat{1}\hat{\sigma}\hat{1}$.

This procedure is performed in several steps.

At the first step, we find the result of the action of the operator $\hat{\sigma}=|g\rangle\langle e|$ on the Jaynes-Cummings functions (8.19.1):

$$\begin{aligned}&\sigma|+,n\rangle=|g\rangle\langle e||+,n\rangle=\cos\varphi_n|g,n-1\rangle,\\ &\sigma|-,n\rangle=|g\rangle\langle e||-,n\rangle=-\sin\varphi_n|g,n-1\rangle\\ &\sigma|-,n\rangle\langle-,n|=-\sin\varphi_n\langle e,n-1|+\cos\varphi_n\langle g,n|=-\sin\varphi_n|g,n-1\rangle\langle-,n|\\ &\sigma|+,n\rangle\langle+,n|=\cos\varphi_n|g,n-1\rangle\langle+,n|,\qquad n=1,2,\ldots;\end{aligned} \tag{8.19.3}$$

The next step is to calculate $\sigma\hat{1}$ in terms of Eq. (8.19.2). For this purpose we employ Eq. (8.19.3) and obtain:

$$\sum_{n=1}^{\infty}\sigma|-,n\rangle\langle-,n| = -\sum_{n=1}^{\infty}\sin\varphi_n|g\rangle|n-1\rangle\langle-,n|$$

$$\sum_{n=1}^{\infty}\sigma|+,n\rangle\langle+,n| = \sum_{n=1}^{\infty}\cos\varphi_n|g\rangle|n-1\rangle\langle+,n|$$

Finally, we obtain:

$$\begin{aligned}\sigma\hat{1} &= |g\rangle\langle e||g,0\rangle\langle g,0| - \sum_{n=1}^{\infty}\sin\varphi_n|g,n-1\rangle\langle-,n| + \sum_{n=1}^{\infty}\cos\varphi_n|g,n-1\rangle\langle+,n| \\ &= \sum_{n=1}^{\infty}(-\sin\varphi_n|g,n-1\rangle\langle-,n| + \cos\varphi_n|g,n-1\rangle\langle+,n|) \\ &= \sum_{n=1}^{\infty}|g,n-1\rangle(-\sin\varphi_n\langle-,n| + \cos\varphi_n\langle+,n|)\end{aligned}$$

Using this expression, we obtain the expansion of the operator $\hat{\sigma} = \hat{1}\hat{\sigma}\hat{1}$ in Jaynes-Cummings eigenfunctions:

$$\begin{aligned}\hat{\sigma} = \hat{I}\hat{\sigma}\hat{I} &= \left(|g,0\rangle\langle g,0| + \sum_{n=1}^{\infty}|-,n\rangle\langle-,n| + \sum_{n=1}^{\infty}|+,n\rangle\langle+,n|\right)\hat{\sigma} \\ &\quad\times\left(|g,0\rangle\langle g,0| + \sum_{n=1}^{\infty}|-,n\rangle\langle-,n| + \sum_{n=1}^{\infty}|+,n\rangle\langle+,n|\right) \\ &= \left(|g,0\rangle\langle g,0| + \sum_{n=1}^{\infty}|-,n\rangle\langle-,n| + \sum_{n=1}^{\infty}|+,n\rangle\langle+,n|\right) \\ &\quad\times\left(\sum_{n=1}^{\infty}|g,n-1\rangle(-\sin\varphi_n\langle-,n| + \cos\varphi_n\langle+,n|)\right) \\ &= \cos\varphi_1|g,0\rangle\langle+,1| - \sin\varphi_1|g,0\rangle\langle-,1| \\ &\quad+\sum_{n=1}^{\infty}(\cos\varphi_n\sin\varphi_{n-1}|+,n-1\rangle\langle+,n| - \sin\varphi_n\sin\varphi_{n-1}|+,n-1\rangle\langle-,n| \\ &\quad+\cos\varphi_n\cos\varphi_{n-1}|-,n-1\rangle\langle+,n| - \sin\varphi_n\cos\varphi_{n-1}|-,n-1\rangle\langle-,n|.\end{aligned} \tag{8.19.4}$$

For brevity, we introduce the following notation:

$$\begin{aligned}
&\hat{S}_{1,n} = |+,n-1\rangle\langle+,n|, \quad \hat{S}_{2,n} = |+,n-1\rangle\langle-,n|,\\
&\hat{S}_{3,n} = |-,n-1\rangle\langle+,n|, \quad \hat{S}_{4,n} = |-,n-1\rangle\langle-,n|,\\
&\hat{S}_{2,1} = |g,0\rangle\langle-,1|, \quad \hat{S}_{1,1} = |g,0\rangle\langle+,1|,\\
&\hat{S}_{1,0} = \hat{S}_{3,0} = \hat{S}_{4,0} = 0
\end{aligned} \tag{8.19.5}$$

The expression (8.19.4) can be rewritten as

$$\begin{aligned}
\hat{\sigma} = \; &\cos\varphi_1 \hat{S}_{1,1} - \sin\varphi_1 \hat{S}_{2,1} + \sum_{n=1}^{\infty} \Big(\cos\varphi_n \sin\varphi_{n-1} \hat{S}_{1,n} - \sin\varphi_n \sin\varphi_{n-1} \hat{S}_{2,n} \\
&+ \cos\varphi_n \cos\varphi_{n-1} \hat{S}_{3,n} - \sin\varphi_n \cos\varphi_{n-1} \hat{S}_{4,n} \Big)
\end{aligned} \tag{8.19.6}$$

Note that operators (8.19.5) have the meaning of transition operators between the Jaynes-Cummings eigenstates. Indeed, if we act, for example, with an operator $\hat{S}_{1,n}$ on the state $|+,n\rangle$, we obtain the state $\hat{S}_{1,n}|+,n\rangle = |+,n-1\rangle\langle+,n||+,n\rangle = |+,n-1\rangle$. Similar relations hold for all other operators from (8.19.5).

Problem 1.20
Obtain the equation for the diagonal and off-diagonal elements, of the density matrix $\hat{\rho}(t)$, assuming that the latter is governed by the Lindblad equation (6.1.4) from the main text.

Solution
First, we expand the density matrix $\hat{\rho}(t)$ over Jaynes-Cummings eigenstates:

$$\begin{aligned}
\hat{\rho} = \; &\rho_{(g,0)(g,0)} |g,0\rangle\langle g,0| \\
&+ \sum_{n=1}^{\infty} \rho_{(g,0)(+,n)} |g,0\rangle\langle+,n| + \sum_{n=1}^{\infty} \rho_{(g,0)(-,n)} |g,0\rangle\langle-,n| \\
&+ \sum_{n=1}^{\infty} \rho_{(+,n)(g,0)} |+,n\rangle\langle g,0| + \sum_{n=1}^{\infty} \rho_{(-,n)(g,0)} |-,n\rangle\langle g,0| \\
&+ \sum_{n_1,n_2=1}^{\infty} \rho_{(+,n_1)(+,n_2)} |+,n_1\rangle\langle+,n_2| + \sum_{n_1,n_2=1}^{\infty} \rho_{(+,n_1)(-,n_2)} |+,n_1\rangle\langle-,n_2| \\
&+ \sum_{n_1,n_2=1}^{\infty} \rho_{(-,n_1)(+,n_2)} |-,n_1\rangle\langle+,n_2| + \sum_{n_1,n_2=1}^{\infty} \rho_{(-,n_1)(-,n_2)} |-,n_1\rangle\langle-,n_2| \Big).
\end{aligned} \tag{8.20.1}$$

From Eq. (6.1.4) from the main text, it follows that the diagonal and off-diagonal terms of the density matrix exhibit independent dynamics. Specifically, from Eqs. (6.1.4) and (3.2.38) from the main text, for diagonal elements, we obtain the following equations:

$$\begin{aligned}\frac{d}{dt}\rho_{(+,n)(+,n)} = &-\gamma_D^{(free)}\cos^2\varphi_n\rho_{(+,n)(+,n)} + \gamma_D^{(free)}\cos^2\varphi_{n+1}\sin^2\varphi_n\rho_{(+,n+1)(+,n+1)}\\ &+\gamma_D^{(free)}\sin^2\varphi_{n+1}\sin^2\varphi_n\rho_{(-,n+1)(-,n+1)},\end{aligned} \tag{8.20.2}$$

$$\begin{aligned}\frac{d}{dt}\rho_{(-,n)(-,n)} = &-\gamma_D^{(free)}\sin^2\varphi_n\rho_{(-,n)(-,n)} + \gamma_D^{(free)}\cos^2\varphi_{n+1}\cos^2\varphi_n\rho_{(+,n+1)(+,n+1)}\\ &+\gamma_D^{(free)}\sin^2\varphi_{n+1}\cos^2\varphi_n\rho_{(-,n+1)(-,n+1)},\end{aligned} \tag{8.20.3}$$

$$\frac{d}{dt}\rho_{(g,0)(g,0)} = \gamma_D^{(free)}\cos^2\varphi_1\rho_{(+,1)(+,1)} + \gamma_D^{(free)}\sin^2\varphi_1\rho_{(-,1)(-,1)}. \tag{8.20.4}$$

One can see that for the dynamics of the diagonal elements, only transitions with a decrease in energy are possible. This is a consequence of our assumption that the free space mode reservoir is at zero temperature.

For the off-diagonal elements, from Eqs. (6.1.4) and (3.2.39) from the main text, we obtain:

$$\frac{d}{dt}\rho_{(+,n_1)(+,n_2)} = \Big(-i(\omega_{+,n_2}-\omega_{+,n_1}) - \gamma_D^{(rad)}\big(\cos^2\varphi_{n_2} + \cos^2\varphi_{n_1}\big)/2\Big)\rho_{(+,n_1)(+,n_2)}, n_1 \neq n_2, \tag{8.20.5}$$

$$\frac{d}{dt}\rho_{(-,n_1)(+,n_2)} = \Big(-i(\omega_{+,n_2}-\omega_{-,n_1}) - \gamma_D^{(rad)}\big(\cos^2\varphi_{n_2} + \sin^2\varphi_{n_1}\big)/2\Big)\rho_{(-,n_1)(+,n_2)}, n_1 \neq n_2, \tag{8.20.6}$$

$$\frac{d}{dt}\rho_{(+,n_1)(-,n_2)} = \Big(-i(\omega_{-,n_2}-\omega_{+,n_1}) - \gamma_D^{(rad)}\big(\sin^2\varphi_{n_2} + \cos^2\varphi_{n_1}\big)/2\Big)\rho_{(+,n_1)(-,n_2)}, n_1 \neq n_2, \tag{8.20.7}$$

$$\frac{d}{dt}\rho_{(-,n_1)(-,n_2)} = \Big(-i(\omega_{-,n_2}-\omega_{-,n_1}) - \gamma_D^{(rad)}\big(\sin^2\varphi_{n_2} + \sin^2\varphi_{n_1}\big)/2\Big)\rho_{(-,n_1)(-,n_2)}, n_1 \neq n_2, \tag{8.20.8}$$

$$\frac{d}{dt}\rho_{(0,g)(+,n)} = \Big(-i\omega_{+,n} - \gamma_D^{(rad)}\cos^2\varphi_n/2\Big)\rho_{(0,g)(+,n)}, \tag{8.20.9}$$

$$\frac{d}{dt}\rho_{(0,g)(-,n)} = \Big(-i\omega_{-,n} - \gamma_D^{(rad)}\sin^2\varphi_n/2\Big)\rho_{(0,g)(-,n)}. \tag{8.20.10}$$

Each off-diagonal element of the density matrix oscillates and simultaneously decays exponentially and independently of other elements.

Problem 1.21
Find the solution to the Lindblad equation with the initial condition, $\hat{\rho}(0) = |g, n_0\rangle\langle g, n_0|$.

Solution
Note that Eqs. (8.20.2)–(8.20.10) are identical with the Lindblad equation; below, we deal with this system of equation instead of the Lindblad equation.

The state $\hat{\rho}(0) = |g, n_0\rangle\langle g, n_0|$ is not an eigenstate of the Jaynes-Cummings Hamiltonian; this state can be represented as the expansion over the Jaynes-Cummings eigenstates (Eq. (2.5.35) from the main text):

$$\begin{aligned}\hat{\rho}(0) &= |g, n_0\rangle\langle g, n_0| = \sin^2\varphi_{n_0}|n, +\rangle\langle n, +| + \cos^2\varphi_{n_0}|n, -\rangle\langle n, -| \\ &+ \sin\varphi_{n_0}\cos\varphi_{n_0}(|n_0, +\rangle\langle n_0, -| + |n_0, -\rangle\langle n_0, +|) \\ &= \rho_{(+,n_0)(+,n_0)}(0)|n, +\rangle\langle n, +| + \rho_{(-,n_0)(-,n_0)}(0)|n, -\rangle\langle n, -| \\ &+ \rho_{(-,n_0)(+,n_0)}|n_0, -\rangle\langle n_0, +| + \rho_{(+,n_0)(-,n_0)}(0)|n_0, +\rangle\langle n_0, -|\end{aligned} \tag{8.21.1}$$

Thus, the initial conditions for Eqs. (8.20.2)–(8.20.10) have the form:

$$\begin{aligned}&\rho_{(+,n_0)(+,n_0)}(0) = \sin^2\varphi_{n_0}, \\ &\rho_{(-,n_0)(-,n_0)}(0) = \cos^2\varphi_{n_0}, \\ &\rho_{(-,n_0)(+,n_0)} = \rho_{(+,n_0)(-,n_0)}(0) = \sin\varphi_{n_0}\cos\varphi_{n_0}, \\ &\rho_{(\pm,n)(\pm,n)}(0) = 0, n > n_0\end{aligned} \tag{8.21.2}$$

with all other elements of the density matrix equal to zero.

Below, we need Eq. (8.21.2) in the limit $\Delta \gg \Omega_R\sqrt{n}$. In this case, $\sin\varphi_n \simeq \varphi_n \simeq \Omega_R\sqrt{n}/|\Delta|$ and $\cos\varphi_n \simeq 1$, and we obtain:

$$\rho_{(n_0,-)(n_0,-)}(0) = 1 \text{ and } \rho_{(+,n_0)(+,n_0)}(0) = \rho_{(-,n_0)(+,n_0)}(0) = \rho_{(+,n_0)(-,n_0)}(0) = 0. \tag{8.21.3}$$

Since the transitions occur due to the interaction with the reservoir of free space modes, and the temperature is assumed to be zero, only transitions with a decrease in the energy (in the n) are possible (see Eq. (8.20.2)). The change in the value of the matrix element $\rho_{(+,n_0,)(+,n_0)}$ can occur due to transitions with greater n. Therefore, since at the initial moment we have $\rho_{(\pm,n)(\pm,n)}(0) = 0$, $n > n_0$, the matrix element $\rho_{(+,n_0,)(+,n_0)}$ is equal to zero all the time.

Now, using the approximations (8.21.3), we start by considering the diagonal elements of the density matrix.

We begin with $n = n_0$. From Eq. (8.20.3) we have:

$$\frac{d}{dt}\rho_{(-,n_0)(-,n_0)}(t) = -\gamma_D^{(rad)}\frac{\Omega_R^2 n}{|\Delta_a|^2}\rho_{(-,n_0)(-,n_0)}(t). \tag{8.21.4}$$

Since $\rho_{(+,n_0)(+,n_0)}(0) = 0$. Further, from Eq. (8.20.3) for $n = n_0 - 1$, we obtain:

$$\dot{\rho}_{(-,n_0-1)(-,n_0-1)}(t) = -\gamma_D^{(rad)}\frac{\Omega_R^2(n-1)}{|\Delta_a|^2}\rho_{(-,n_0-1)(-,n_0-1)}(t) + \gamma_D^{(rad)}\frac{\Omega_R^2 n}{|\Delta_a|^2}\rho_{(-,n_0)(-,n_0)}(t). \tag{8.21.5}$$

Next, we consider equation (8.20.2) for $\rho_{(+,n_0-1)(+,n_0-1)}(t)$. From this equation and using $\rho_{(+,n_0)(+,n_0)}(t) = 0$, we obtain:

$$\dot{\rho}_{(+,n_0-1)(+,n_0-1)}(t) = -\gamma_D^{(rad)}\rho_{(+,n_0-1)(+,n_0-1)}(t) + \gamma_D^{(rad)}\frac{\Omega_R^4 n(n-1)}{|\Delta|^4}\rho_{(-,n_0)(-,n_0)}(t), \tag{8.21.6}$$

The factor $\Omega_R^4 n(n-1)/|\Delta|^4$ is of the second order of smallness with respect to the parameter $\Omega_R^2 n/|\Delta_a|^2 \ll 1$. Therefore, in Eq. (8.21.6), we neglect the term $\left(\gamma_D^{(rad)}\Omega_R^4 n(n-1)/|\Delta|^4\right)\rho_{(-,n_0)(-,n_0)}$. Then, solution (8.21.6) is $\rho_{(+,n_0-1)(+,n_0-1)}(t) = 0$.

Repeating the above arguments for the elements $\rho_{(+,n)(+,n)}$, $n < n_0 - 1$, of the density matrix, we obtain that $\rho_{(+,n)(+,n)}(t) = 0$ for any n.

At the same time, for $\rho_{(-,n)(-,n)}(t)$, $n < n_0 - 1$, we obtain the equation of the same form as Eq. (8.21.5). For brevity, let us denote $\rho_{(n,-)(n,-)}(t) \equiv p_n(t)$, $\gamma_D^{(rad)}\Omega_R^2 n/|\Delta_a|^2 \equiv \gamma_n$, and $\omega_{n,-} = \omega_n$. The quantity $p_n(t)$ has the meaning of the probability of the occupation of the entangled state of the selected mode and the atom $|-,n\rangle = -\sin\varphi_n|e,n-1\rangle + \cos\varphi_n|g,n\rangle$, while γ_n has the meaning of the transition rate form the state $|-,n\rangle$ to the state $|-,n-1\rangle$. From Eq. (8.21.4) we obtain equations for $p_n(t)$:

$$\begin{aligned}
&\frac{d}{dt}p_{n_0}(t) = -\gamma_{n_0}p_{n_0}\\
&\frac{d}{dt}p_n(t) = -\gamma_n p_n(t) + \gamma_{n+1}p_{n+1}(t), \qquad 1 \le n < n_0\\
&\frac{d}{dt}p_0(t) = \gamma_1 p_1(t)
\end{aligned} \tag{8.21.7}$$

with the initial condition

$$p_{n_0}(0)=1,\ \ p_n(0)=0, 0\le n<n_0. \tag{8.21.8}$$

These are Eqs. (6.1.8) and (6.1.9) of the main text.

Problem 1.22
Derive Eq. (6.1.10):

$$\left\langle \hat{\sigma}^\dagger(t+\tau)\hat{\sigma}(t)\right\rangle \simeq \sum_{k=n_0}^{1}\left(\Omega_R^2 k/|\Delta_a|^2\right)p_k(t)\exp((i\omega_a-(\gamma_k+\gamma_{k-1})/2)\tau)$$

Solution
As shown in Sect. 3.2.5 (see also Problem 1.9), to calculate the two-time correlator

$$\left\langle \hat{\sigma}_H^\dagger(t+\tau)\hat{\sigma}_H(t)\right\rangle = \mathrm{Tr}_S\left(\hat{\sigma}_{Schr}^\dagger \hat{P}_L(t+\tau;t)\left[\left(\hat{\sigma}_{Schr}\hat{P}_L(t;0)[\rho_S(0)]\right)\right]\right),$$

one needs to solve the Lindblad equation twice.

First, we need to find $\hat{\rho}(t)$. As has been shown in Problem 1.21, the density matrix can be approximately presented in the form:

$$\rho(t)\equiv \hat{P}_L(t;0)[\rho_S(0)]\simeq \sum_n p_n(t)|-,n\rangle\langle -,n| \tag{8.22.1}$$

if the initial condition is $\hat{\rho}(0)=|g,n_0\rangle\langle g,n_0|$ and $\Omega_R^2 k/|\Delta_a|^2\ll 1$. It means that we disregard off-diagonal elements. The evolution of $p_n(t)$ is determined by Eq. (8.21.7), solutions to which are equivalent to the solutions to the Lindblad equation (see Sect. 3.2.2 and Problem 1.21). To solve these equations, we need to find $\hat{\sigma}\hat{\rho}(t)$:

$$\begin{aligned}
\hat{\sigma}\hat{\rho}(t) &\simeq \sum_n p_n(t)\hat{\sigma}|-,n\rangle\langle -,n| = \sum_n p_n(t)\hat{\sigma}(-\sin\varphi_n|e,n-1\rangle+\cos\varphi_n|g,n\rangle)\langle -,n| \\
&= -\sum_n p_n(t)\sin\varphi_n|g,n-1\rangle\langle -,n| \\
&= -\sum_n p_n(t)\sin\varphi_n(\sin\varphi_n|+,n-1\rangle+\cos\varphi_n|-,n-1\rangle)\langle -,n| \\
&\simeq -\sum_n p_n(t)\sin\varphi_n|-,n-1\rangle\langle -,n|
\end{aligned} \tag{8.22.2}$$

where, in the last step, we have used that $\sin\varphi_n \ll \cos\varphi_n$ and $\cos\varphi_n\simeq 1$.

At the second step, we have to solve the Lindblad equation up to time $t+\tau$, using $\hat{\sigma}\hat{\rho}(t)$ (see Eq. (8.22.2)) as the initial condition (see Eq. (3.2.62)).

Since the initial conditions differ from the one considered above, we should derive the proper algorithm. Note that in Eq. (8.22.2), only off-diagonal

elements $|-,n-1\rangle\langle -,n|$ of the density matrix are present. In Problem 1.20, the dynamics of the amplitude of the off-diagonal elements of the density matrix is found; see Eqs. (8.20.5)–(8.20.10). Particularly, the amplitude of the off-diagonal element $|-,n-1\rangle\langle -,n|$ evolves according to Eq. (8.20.8). Using this equation, we can write the solution to the Lindblad equation with the initial condition (8.22.2) in the form:

$$\begin{aligned}
&\widehat{\widetilde{\rho}}(t+\tau)\simeq\\
&\quad\simeq-\sum_n p_n(t)e^{\left(-i(\omega_{-,n-1}-\omega_{-,n})-\gamma_D^{(rad)}\left(\sin^2\varphi_{n_2}+\sin^2\varphi_{n_1}\right)/2\right)\tau}\sin\varphi_n|-,n-1\rangle\langle -,n|\\
&\quad\simeq-\sum_n p_n(t)\exp((i\omega_a-(\gamma_n+\gamma_{n-1})/2)\tau)\sin\varphi_n|-,n-1\rangle\langle -,n|
\end{aligned}\tag{8.22.3}$$

At the last step, we take into account that $\omega_{-,n-1}-\omega_{-,n}\simeq-\omega_a$ (see Eq. (6.1.6) in the main text) and use the notation $\gamma_n=\gamma_D^{(rad)}\sin^2\varphi_n\simeq\gamma_D^{(rad)}\Omega_R^2 n/|\Delta_a|^2$ (see the paragraph before Eq. (6.1.8) in the main text).

The final step is calculating $\mathrm{Tr}\left(\hat{\sigma}^\dagger\widehat{\widetilde{\rho}}(t+\tau)\right)$. Substituting Eq. (8.22.3) into the expression $\mathrm{Tr}\left(\hat{\sigma}^\dagger\widehat{\widetilde{\rho}}(t+\tau)\right)$, we obtain:

$$\begin{aligned}
&\mathrm{Tr}\left(\hat{\sigma}^\dagger\widehat{\widetilde{\rho}}(t+\tau)\right)\\
&\quad=\mathrm{Tr}\left(-\sum_n p_n(t)\exp((i\omega_a-(\gamma_n+\gamma_{n-1})/2)\tau)\sin\varphi_n\hat{\sigma}^\dagger|-,n-1\rangle\langle -,n|\right)
\end{aligned}\tag{8.22.4}$$

Further, we use explicit expression (8.5.16) for the Jaynes-Cummings state:

$$\begin{aligned}
&\mathrm{Tr}\left(\hat{\sigma}^\dagger\widehat{\widetilde{\rho}}(t+\tau)\right)=\\
&\quad=\mathrm{Tr}\Bigg(-\sum_n p_n(t)\exp((i\omega_a-(\gamma_n+\gamma_{n-1})/2)\tau)\sin\varphi_n\\
&\qquad\times\hat{\sigma}^\dagger(\cos\varphi_n|g,n-1\rangle-\sin\varphi_n|e,n-2\rangle)\langle -,n|\Bigg)\\
&\quad=\mathrm{Tr}\left(-\sum_n p_n(t)\exp((i\omega_a-(\gamma_n+\gamma_{n-1})/2)\tau)\sin\varphi_n\cos\varphi_n|e,n-1\rangle\langle -,n|\right)
\end{aligned}\tag{8.22.5}$$

At the second step, we express the state $|e,n-1\rangle$ through the Jaynes-Cummings state as $|e,n-1\rangle=\cos\varphi_n|+,n\rangle-\sin\varphi_n|-,n\rangle$. As a result, we obtain:

$$\mathrm{Tr}\left(\hat{\sigma}^{\dagger}\widehat{\tilde{\rho}}(t+\tau)\right) =$$
$$= \mathrm{Tr}\left(-\sum_n p_n(t)\exp((i\omega_a - (\gamma_n+\gamma_{n-1})/2)\tau)\sin\varphi_n(\cos\varphi_n|+n\rangle - \sin\varphi_n|-n\rangle)\langle -n|\right) \tag{8.22.6}$$

Finally, we explicitly calculate the trace as a sum of diagonal elements over Jaynes-Cummings state:

$$\begin{aligned}
&\mathrm{Tr}\left(\hat{\sigma}^{\dagger}\widehat{\tilde{\rho}}(t+\tau)\right)\\
&= \mathrm{Tr}\left(-\sum_n p_n(t)\exp((i\omega_a - (\gamma_n+\gamma_{n-1})/2)\tau)\sin\varphi_n(\cos\varphi_n|+,n\rangle - \sin\varphi_n|-,n\rangle)\langle -,n|\right)\\
&= \langle -,n|\left(-\sum_n p_n(t)\exp((i\omega_a - (\gamma_n+\gamma_{n-1})/2)\tau)\sin\varphi_n\right.\\
&\quad \left.\times(\cos\varphi_n|+,n\rangle - \sin\varphi_n|-,n\rangle)\langle -,n||-,n\rangle\right.\\
&\quad +\langle +,n|\left(-\sum_n p_n(t)\exp((i\omega_a - (\gamma_n+\gamma_{n-1})/2)\tau)\sin\varphi_n\right.\\
&\quad \left.\times(\cos\varphi_n|+,n\rangle - \sin\varphi_n|-,n\rangle)\langle -,n||+,n\rangle\right.\\
&= \sum_n p_n(t)\exp((i\omega_a - (\gamma_n+\gamma_{n-1})/2)\tau)\sin^2\varphi_n\\
&\approx \sum_1^{n_0}\left(\Omega_a^2 k/|\Delta_a|^2\right)p_k(t)\exp((i\omega_a - (\gamma_k+\gamma_{k-1})/2)\tau)
\end{aligned} \tag{8.22.7}$$

This is Eq. (6.1.10) from the main text.

Problem 1.23
Derive the expression for the expectation value $\langle\hat{\sigma}(t)\rangle$ (Eq. (6.2.15)).

Solution
Recall that we consider the case of the coherent initial state $|g,\alpha\rangle$, then

$$\hat{\rho}(0) = \exp\left(-|\alpha|^2/2\right)\sum_{n_1=0}^{\infty}\left(\alpha^{n_1}/\sqrt{n_1!}\right)|g,n_1\rangle\langle g,\alpha|,$$

where $|\alpha\rangle = \exp\left(-|\alpha|^2/2\right)\sum_{n=0}^{\infty}\left(\alpha^n/\sqrt{n!}\right)|n\rangle$ is the coherent state of the field (see Problem 1.17). The expansion of such an initial state over the Jaynes-Cummings eigenstates has the form:

$$\hat{\rho}(0) = \exp\Big(-|\alpha|^2\Big)\Bigg[|g0\rangle\langle g0| + + \sum_{n_1=1}^{\infty}\Bigg(\sin\varphi_{n_1}\frac{\alpha^{n_1}}{\sqrt{n_1!}}|+n_1\rangle\langle g0|$$
$$+\cos\varphi_{n_1}\frac{\alpha^{n_1}}{\sqrt{n_1!}}|-n_1\rangle\langle g0|\Bigg) + \sum_{n_2=1}^{\infty}\Bigg(\sin\varphi_{n_2}\frac{\alpha^{*n_2}}{\sqrt{n_2!}}|g0\rangle\langle+n_2|$$
$$+\cos\varphi_{n_2}\frac{\alpha^{*n_2}}{\sqrt{n_2!}}|g0\rangle\langle-n_2|\Bigg) + \sum_{n_1,n_2=1}^{\infty}\Bigg(\sin\varphi_{n_1}\sin\varphi_{n_2}\frac{\alpha^{n_1}}{\sqrt{n_1!}}\frac{\alpha^{*n_2}}{\sqrt{n_2!}}|+n_1\rangle\langle+n_2|$$
$$+\sin\varphi_{n_1}\cos\varphi_{n_2}\frac{\alpha^{n_1}}{\sqrt{n_1!}}\frac{\alpha^{*n_2}}{\sqrt{n_2!}}|+n_1\rangle\langle-n_2|$$
$$+\cos\varphi_{n_1}\sin\varphi_{n_2}\frac{\alpha^{n_1}}{\sqrt{n_1!}}\frac{\alpha^{*n_2}}{\sqrt{n_2!}}|-n_1\rangle\langle+n_2|$$
$$+\cos\varphi_{n_1}\cos\varphi_{n_2}\frac{\alpha^{n_1}}{\sqrt{n_1!}}\frac{\alpha^{*n_2}}{\sqrt{n_2!}}|-n_1\rangle\langle-n_2|\Bigg)\Bigg] \tag{8.23.1}$$

In expansion (8.23.1) of the density matrix over eigenstates, there are all kinds of off-diagonal elements. Equation (6.1.2) from the main text shows that to calculate the average dipole moment, we need to know the dynamics of not all off-diagonal matrix elements, but only $\rho_{(g,0)(+,1)}$, $\rho_{(+,n-1)(+,n)}$, $\rho_{(-,n-1)(+,n)}$, and $\rho_{(-,n-1)(-,n)}$. According to Eqs. (8.20.5)–(8.20.10) from Problem 1.20, these matrix elements obey the equations:

$$\dot{\rho}_{(+,n-1)(+,n)} = \left(-i(\omega_{+,n}-\omega_{+,n-1}) - \frac{\gamma_D^{(rad)}}{2}\left(\cos^2\varphi_n + \cos^2\varphi_{n-1}\right)\right)\rho_{(+,n-1)(+,n)}, \tag{8.23.2}$$

$$\dot{\rho}_{(-,n-1)(+,n)} = \left(-i(\omega_{+,n}-\omega_{-,n-1}) - \frac{\gamma_D^{(rad)}}{2}\left(\cos^2\varphi_n + \sin^2\varphi_{n-1}\right)\right)\rho_{(-,n-1)(+,n)}, \tag{8.23.3}$$

$$\dot{\rho}_{(+,n-1)(-,n)} = \left(-i(\omega_{-,n}-\omega_{+,n-1}) - \frac{\gamma_D^{(rad)}}{2}\left(\sin^2\varphi_n + \cos^2\varphi_{n-1}\right)\right)\rho_{(+,n-1)(-,n)}, \tag{8.23.4}$$

$$\dot{\rho}_{(-,n-1)(-,n)} = \left(-i(\omega_{-,n}-\omega_{-,n-1}) - \frac{\gamma_D^{(rad)}}{2}\left(\sin^2\varphi_n + \sin^2\varphi_{n-1}\right)\right)\rho_{(-,n-1)(-,n)}, \tag{8.23.5}$$

$$\dot{\rho}_{(0,g)(+,1)} = \left(-i\omega_{+,1} - \gamma_D^{(rad)} \cos^2\varphi_1/2\right)\rho_{(0,g)(+,1)}, \tag{8.23.6}$$

$$\dot{\rho}_{(0,g)(-,1)} = \left(-i\omega_{-,1} - \gamma_D^{(rad)} \sin^2\varphi_1/2\right)\rho_{(0,g)(-,1)}, \tag{8.23.7}$$

and in accordance with Eq. (8.23.1), the initial conditions of these matrix elements have the form:

$$\rho_{(+,n-1)(+,n)}(0) = \exp\left(-|\alpha|^2\right) \sin\varphi_n \sin\varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}}, \tag{8.23.8}$$

$$\rho_{(-,n-1)(+,n)}(0) = \exp\left(-|\alpha|^2\right) \cos\varphi_n \sin\varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}}, \tag{8.23.9}$$

$$\rho_{(+,n-1)(-,n)}(0) = \exp\left(-|\alpha|^2\right) \sin\varphi_n \cos\varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}}, \tag{8.23.10}$$

$$\rho_{(-,n-1)(-,n)}(0) = \exp\left(-|\alpha|^2\right) \cos\varphi_n \cos\varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}}, \tag{8.23.11}$$

$$\rho_{(0,g)(+,1)}(0) = \exp\left(-|\alpha|^2\right) \sin\varphi_1 \frac{\alpha^*}{\sqrt{1!}}, \tag{8.23.12}$$

$$\rho_{(0,g)(-,1)}(0) = \exp\left(-|\alpha|^2\right) \cos\varphi_1 \frac{\alpha^*}{\sqrt{1!}}. \tag{8.23.13}$$

Solutions (8.23.2)–(8.23.7) with initial conditions (8.23.8)–(8.23.13) are

$$\rho_{(+,n-1)(+,n)}(t) = e^{-|\alpha|^2} \sin\varphi_n \sin\varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}} e^{\left(-i(\omega_{+,n}-\omega_{+,n-1}) - \frac{\gamma_D^{(rad)}}{2}\left(\cos^2\varphi_n + \cos^2\varphi_{n-1}\right)\right)t}, \tag{8.23.14}$$

$$\rho_{(-,n-1)(+,n)}(t) = e^{-|\alpha|^2} \cos\varphi_n \sin\varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}} e^{\left(-i(\omega_{+,n}-\omega_{-,n-1}) - \frac{\gamma_D^{(rad)}}{2}\left(\cos^2\varphi_n + \sin^2\varphi_{n-1}\right)\right)t}, \tag{8.23.15}$$

$$\rho_{(+,n-1)(-,n)}(t) = e^{-|\alpha|^2} \sin\varphi_n \cos\varphi_{n-1} \frac{\alpha^{n-1}}{\sqrt{(n-1)!}} \frac{\alpha^{*n}}{\sqrt{n!}} e^{\left(-i(\omega_{-,n}-\omega_{+,n-1}) - \frac{\gamma_D^{(rad)}}{2}\left(\sin^2\varphi_n + \cos^2\varphi_{n-1}\right)\right)t}, \tag{8.23.16}$$

$$\rho_{(-,n-1)(-,n)}(t)=e^{-|\alpha|^2}\cos\varphi_n\cos\varphi_{n-1}\frac{\alpha^{n-1}}{\sqrt{(n-1)!}}\frac{\alpha^{*n}}{\sqrt{n!}}e^{\left(-i(\omega_{-,n}-\omega_{-,n-1})-\frac{\gamma_D^{(rad)}}{2}\left(\sin^2\varphi_n+\sin^2\varphi_{n-1}\right)\right)t},\tag{8.23.17}$$

$$\rho_{(0,g)(+,1)}(t)=e^{-|\alpha|^2}\sin\varphi_1\frac{\alpha^*}{\sqrt{1!}}e^{\left(-i\omega_{+,1}-\gamma_D^{(rad)}\cos^2\varphi_1/2\right)t},\tag{8.23.18}$$

$$\rho_{(0,g)(-,1)}(t)=e^{-|\alpha|^2}\cos\varphi_1\frac{\alpha^*}{\sqrt{1!}}e^{\left(-i\omega_{-,1}-\gamma_D^{(rad)}\sin^2\varphi_1/2\right)t}.\tag{8.23.19}$$

Substituting Eqs. (8.23.14)–(8.23.19) into the expression for the dipole moment (see Eq. (6.2.13) from the main text), we obtain:

$$\begin{aligned}\langle\hat{\sigma}(t)\rangle = e^{-|\alpha|^2}\Bigg[&\cos\varphi_1\sin\varphi_1\frac{\alpha^*}{\sqrt{1!}}\exp\left(\left(-i\omega_{+,1}-\gamma_D^{(rad)}\cos^2\varphi_1/2\right)t\right)\\
&-\sin\varphi_1\cos\varphi_1\frac{\alpha^*}{\sqrt{1!}}\exp\left(\left(-i\omega_{-,1}-\gamma_D^{(rad)}\sin^2\varphi_1/2\right)t\right)\\
&+\sum_{n=2}^{\infty}\frac{\alpha^{n-1}}{\sqrt{(n-1)!}}\frac{\alpha^{*n}}{\sqrt{n!}}\left(\cos\varphi_n\sin^2\varphi_{n-1}\sin\varphi_n\right.\\
&\times\exp\left(\left(-i(\omega_{+,n}-\omega_{+,n-1})-\frac{\gamma_D^{(rad)}}{2}\left(\cos^2\varphi_n+\cos^2\varphi_{n-1}\right)\right)t\right)\\
&-\sin^2\varphi_n\sin\varphi_{n-1}\cos\varphi_{n-1}\exp\left(\left(-i(\omega_{-,n}-\omega_{+,n-1})\right.\right.\\
&\left.\left.-\frac{\gamma_D^{(rad)}}{2}\left(\sin^2\varphi_n+\cos^2\varphi_{n-1}\right)\right)t\right)+\cos^2\varphi_n\cos\varphi_{n-1}\sin\varphi_{n-1}\\
&\exp\left(\left(-i(\omega_{+,n}-\omega_{-,n-1})-\frac{\gamma_D^{(rad)}}{2}\left(\cos^2\varphi_n+\sin^2\varphi_{n-1}\right)\right)t\right)\\
&-\sin\varphi_n\cos^2\varphi_{n-1}\cos\varphi_n e\left(\left(-i(\omega_{-,n}-\omega_{-,n-1})\right.\right.\\
&\left.\left.\left.-\frac{\gamma_D^{(rad)}}{2}\left(\sin^2\varphi_n+\sin^2\varphi_{n-1}\right)\right)t\right)\right)\Bigg].\end{aligned}\tag{8.23.20}$$

In the limit of large frequency detuning, $\Omega_{\mathrm{R}}^2|\alpha|^2/\Delta_a^2\ll 1$, the quantities $\Omega_{\mathrm{R}}^2|\alpha|^2/\Delta^2$ and $\sin\varphi_n\simeq\Omega_R\sqrt{n}/|\Delta_a|$ are small parameters, while $\cos\varphi_n\simeq 1$. Therefore, the main contribution to sum (8.23.20) is made by the first, second, fifth, and sixth terms, which are proportional to the first power of the small parameter.

Further, the decay rates of the first and fifth terms are $\gamma_D^{(rad)}\cos^2\varphi_1/2 \simeq \gamma_D^{(rad)}/2$ and $\gamma_D^{(rad)}\left(\cos^2\varphi_n + \sin^2\varphi_{n-1}\right)/2 \simeq \gamma_D^{(rad)}/2$, respectively. Thus, on the time scale $t \gg \gamma_0^{-1}$, these terms are equal to zero. In turn, the decay rates of the second and six terms are $\gamma_D^{(rad)}\sin^2\varphi_1/2 \simeq \gamma_D^{(rad)}\Omega_R^2 n/2|\Delta_a|^2 \ll \gamma_D^{(rad)}$ and $\gamma_D^{(rad)}\left(\sin^2\varphi_n + \sin^2\varphi_{n-1}\right)/2 \simeq \gamma_D^{(rad)}\Omega_R^2 n/|\Delta_a|^2 \ll \gamma_D^{(rad)}$, respectively. Thus, we conclude that on the time scale $t \gg \gamma_0^{-1}$, the second and sixth terms give the main contribution to Eq. (8.23.20):

$$\langle\hat{\sigma}(t)\rangle = -\frac{e^{-i\omega_{ext}t}\Omega_R}{|\Delta_a|}e^{-|\alpha|^2}\left[\frac{\alpha^*}{\sqrt{1!}}\exp\left(-\left(\gamma_D^{(rad)}\Omega_R^2 n/2|\Delta|^2\right)t\right)\right.$$
$$\left. + \sum_{n=2}^{\infty}\sqrt{n}\frac{\alpha^{n-1}}{\sqrt{(n-1)!}}\frac{\alpha^{*n}}{\sqrt{n!}}\exp\left(-\left(\gamma_D^{(rad)}\Omega_R^2 n/|\Delta|^2\right)t\right)\right]. \tag{8.23.21}$$

Now, assuming that the condition for the nonresonant excitation $\Omega_R^2|\alpha|^2/|\Delta_a|^2 \ll 1$ remains true, we consider the limit of a large amplitude of the exciting field, $|\alpha|^2 \gg 1$. Since, in this case, the main contribution to sum (8.23.21) is made by the terms for which $n \simeq |\alpha|^2$, we can calculate this sum approximately. Assuming that inside the sum, the value $\sqrt{n}$ is slowly changing and replacing it with the value $\sqrt{n} \simeq |\alpha|$, we obtain:

$$\langle\hat{\sigma}(t)\rangle \simeq -\frac{e^{-i\omega_{ext}t}\Omega_R|\alpha|}{|\Delta_a|}e^{-|\alpha|^2}\sum_{n=0}^{\infty}\frac{|\alpha|^{2n}}{n!}e^{-\left(\gamma_D^{(rad)}\Omega_R^2 n/|\Delta_a|^2\right)t}$$
$$= e^{|\alpha|^2\left(e^{-\left(\gamma_D^{(rad)}\Omega_R^2/|\Delta_a|^2\right)t}-1\right)}\frac{e^{-i\omega_{ext}t}\Omega_R|\alpha|}{|\Delta_a|}. \tag{8.23.22}$$

Next, we consider times at which the field amplitude in the selected mode remains almost unchanged, i.e., times $t \ll \left(\gamma_D^{(rad)}\Omega_R^2/|\Delta_a|^2\right)^{-1}$. Then, Eq. (8.23.22) is simplified:

$$\langle\hat{\sigma}(t)\rangle \simeq \frac{e^{-i\omega_{ext}t}\Omega_R|\alpha|}{|\Delta_a|}\exp\left(-\frac{|\alpha|^2\gamma_D^{(rad)}\Omega_R^2}{|\Delta_a|^2}t\right). \tag{8.23.23}$$

which is identical to Eq. (6.2.14) from the main text.

Part II
The Raman Effect

Chapter 9
Introduction

In the first part, we considered the elastic scattering of light by atoms. Our approach is based on the concept that a scatterer (an atom or a molecule) and incident photons belonging to the selected EM mode form a closed system—a "dressed" atom with its own stationary states. Without interacting with the reservoir of free space modes, the dressed atom can neither emit nor absorb additional photons. It is the EM field of free space modes that causes transitions between the dressed atom eigenstates.

We also have seen that only a continuum of degrees of freedom of the reservoir makes irreversible transitions between the states of an atom possible. Therefore, we focus on reservoirs containing a continuum of modes.

The reservoir modes can couple with each other via the atom. Since dealing with a continuum of unknowns is difficult, we split the problem into two parts. First, we study the variables belonging to the atom. The system of equations for these variables is not closed because the dressed atom interacts with the reservoir of free space modes. At this stage, we assume that the reservoir is in equilibrium. After excluding the reservoir variables, we obtain new equations for the atom variables. Depending on whether we work in the Heisenberg or Schrödinger pictures, these are either Heisenberg-Langevin or Lindblad equations. In these equations, the action of the reservoir on the atom is described by dissipative and noise terms. The solution to the resulting equation describes the relaxation of the dressed atom state. Second, we focus our attention on the reservoir. During the relaxation, the dressed atom exchanges photons with the reservoir of free space modes. Substituting the dressed atom variables obtained at the first step into equations for free space modes, we calculate the disturbances of the modes, which represent a spectrum of scattered radiation.

In the second part of the book, the approach described in Part I is applied to inelastic light scattering. Unlike elastic (Rayleigh) scattering, during inelastic scattering, the frequency of the scattered light differs from that of the incident light. Such a frequency change occurring due to the change in the kinetic energy of the atom was considered by Compton [1].

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Smekal [2] was the first to consider the inelastic scattering of photons associated with a change in the internal energy of the atom, along with a change in its kinetic energy. He assumed that the change in the atom's internal energy is caused by nonradiative transitions of the atom between electronic eigenstates (see also Ref. [3]). This work was often cited as a prediction of the Raman effect [4–13]. Without diminishing the importance of Smekal's work, in which he predicted the off-resonant excitation of the atom and the need to take into account atom's recoil during radiation, we emphasize that Smekal's effect should also be observed for isolated atoms. Essentially, Smekal did not provide any indication that intramolecular vibrations of atoms might cause inelastic scattering. The effect of such vibrations on light scattering is associated with the name of Indian physicist C.V. Raman, who was the first to observe it in gases and liquids [9].

Raman initially set out to experimentally validate the theory of the Compton effect in optics. However, rather than observing the anticipated weak optical effect, he discovered a more prominent phenomenon. In Raman's experiments, it was "shown that in every case in which light is scattered by the molecules in dust-free liquids or gases, the diffuse (scattered) radiation of the ordinary kind, having the same wavelength as the incident beam, is accompanied by a modified scattered radiation of degraded frequency" [8–10]. (The line observed by Raman is called the Stokes line.)

Concurrently with the Raman group, in the Soviet Union, Mandelstam and Landsberg worked on the closely related problem of detecting the *fine structure* in the Rayleigh spectrum of light scattered by solids. They assumed that such a fine structure was due to the modulation of scattered light by elastic thermal waves, in accordance with the Debye theory. Specifically, Landsberg and Mandelstam studied the scattering of the mercury lamp light by a quartz crystal. They reported [6] that in the scattering spectrum, each line of the spectrum of mercury is accompanied by a couple of weak satellites—one with the violet shift (the anti-Stokes line) and the other one with the red shift (the Stokes line) (see Fig. 9.1). They expressed doubts about the connection between their and Raman's results but offered no explanation for their observations. They only suggested that the phenomenon must be of a quantum nature because they conducted experiments at low temperatures compared to the energy of the observed quanta.

Raman's works instantly evoked a response in the world scientific community. In France, Rocard's and Cabannes' groups looked for the Raman effect using a low-power installation [4, 5, 11]. However, the works of these groups only contained some theoretical ideas about the phenomenon, attributing this novel effect to optical modulation by the oscillating molecule. In Ref. [11], the effect was described as "optical beating." Importantly, in these works, the Raman effect associated with the pure rotational motion of molecules was predicted.

In the United States, Wood investigated resonant light emission in various materials. After Raman published his paper, Wood looked through his previously obtained photographic plates and found additional red-shifted lines similar to Raman's. He also observed the lines with violet shift in frequencies [12]. Wood introduced the term "anti-Stokes" for scattered light, whose quanta have higher energy than the incident light.

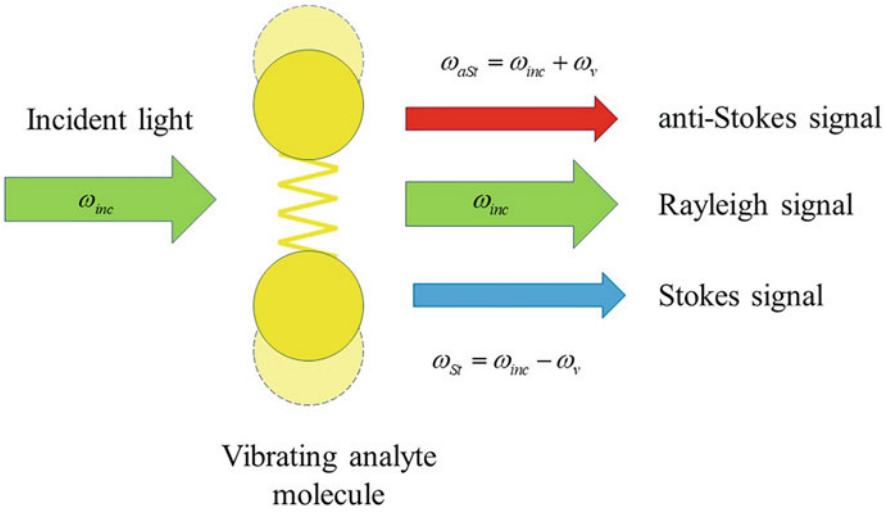

Fig. 9.1 Light scattering by a vibrating analyte molecule that is considered as a harmonic oscillator with the eigenfrequency ω_v

In the Raman effect, the scattered light spectrum is characterized by two satellite lines equidistantly shifted from the centerline by the so-called Stokes frequency shifts [14–33]. The centerline is associated with the elastic Rayleigh scattering. The shifts are small compared to the frequency of the incident wave and the frequencies of optical transitions in a molecule. Since the shifts do not depend on the frequency of the incident light, they have been associated with some "hidden" vibrational states of the molecule.

"Hidden" implies that the vibration of nuclei in a molecule cannot be directly excited by infrared (IR) radiation. The matrix elements of dipole moments between the vibrational states are assumed to be zero. Such a molecule is referred to as Raman-active. When the matrix elements of the dipole moment between the molecule vibrational states are nonzero, the vibrational states can be excited by IR radiation. Such molecules are called IR-active.

According to the classical theory, the modulation of the dipole moment leads to the emergence of two sidelines. If a nonpolar molecule is placed in an external electric field **E**, positive and negative charges move in opposite directions, inducing a dipole moment **d**, which should be modulated by low-frequency oscillations of atoms inside a molecule. If the electric field of such a dipole is weak compared to intramolecular fields, the displacements of charges are small, and the resulting dipole moment is proportional to the external field:

$$\mathbf{d} = \alpha \mathbf{E},$$

where α is the molecule polarizability.

Since the induced dipole moment oscillates with the frequency of the external field ω_{ext}, it radiates light of the same frequency (Rayleigh scattering). When the scatterer is a molecule, we have to take into account the possible vibrations of nuclei in the molecule. Since the nuclear mass is about 2000 times greater than that of an electron, the mobility of electrons is much greater than that of nuclei. In experiments on the Raman scattering, the characteristic frequency ω_v of nucleus oscillations in molecules is much smaller than the frequency ω_{ext} of the incident field, and the electrons have time to adjust to the change in the positions of nuclei. Consequently, the electronic polarizability of the molecule is periodically modulated:

$$\alpha = \alpha_0 + \alpha_1 \sin(\omega_v t)$$

causing oscillations of the dipole moment

$$\begin{aligned} d = \alpha E &= \alpha_0 E \sin(\omega_{ext} t) + \alpha_1 E \sin(\omega_v t) \sin(\omega_{ext} t) \\ &= \alpha_0 E \sin(\omega_{ext} t) + \alpha_1 E[\cos(\omega_{ext} - \omega_v)t - \cos(\omega_{ext} + \omega_v)t]. \end{aligned} \tag{9.1.1}$$

The last term in this equation corresponds to the two sidelines in the radiation spectrum of the dipole moment. These sidelines are equidistant from the frequency ω_{ext}, and their frequencies, $\omega_{ext} - \omega_v$ and $\omega_{ext} + \omega_v$, determine the Stokes and anti-Stokes lines, respectively [13]. Equation (9.1.1) shows that the emergence of sidelines in Raman scattering can be associated with the parametric modulation of the electronic subsystem of the molecule by nucleus vibrations. Below, we show that the consistent quantum mechanical description confirms the parametric nature of the Raman scattering. According to Eq. (9.1.1), the intensities of the sidelines should be identical. Experiments, however, show that the Stokes signal is much stronger than the anti-Stokes.

To explain the difference between the amplitudes of the Stokes and anti-Stokes scattering, the methods of quantum mechanics are required. According to the Bohr theory of atoms, no radiation arises when an electron is at a certain energy level. The radiation only occurs when the electron "jumps" from one unperturbed quantum level corresponding to the energy E_1 to another unperturbed level with the lower energy E_2. The released energy $\Delta = E_1 - E_2$ is assumed to be emitted as a photon with the energy $\hbar\omega = \Delta$. The interaction of light and an atom is considered as an act of resonant absorption or emission of a photon during the transition of the atom from one eigenstate to another. This picture served as the basis for creating the theory of spectroscopy.

Based on the Bohr theory of transitions between quantum states, the quantum mechanical description of Raman scattering faced some technical and fundamental difficulties. The technical problem is tied to the necessity of taking into account vibrations of the molecule nuclei. By the time of the discovery of Raman scattering, the quantum theory of vibrational and rotational spectra in molecules was still under development (see Ref. [34] and references therein). Unifying this theory with the theory of optical transitions is a very cumbersome problem that still does not have a

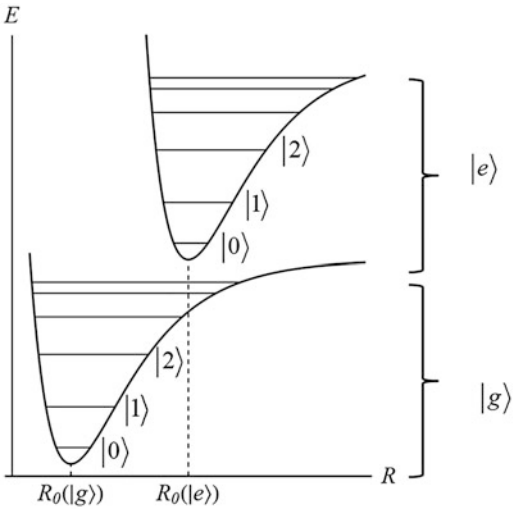

Fig. 9.2 Potential energy curves for the ground $|g\rangle$ and excited $|e\rangle$ electronic states of a diatomic molecule: $R_0(|g\rangle)$ and $R_0(|e\rangle)$ are the equilibrium distance between the nuclei of the molecule in the ground and excited electronic states, respectively; $|0\rangle$, $|1\rangle$, $|2\rangle$ are the vibron levels

rigorous general solution. One of the most important simplifications of this problem comes from the application of the adiabatic approximation, which, for quantum mechanics, was developed by Born and Oppenheimer [34]. Applying this approximation, we can solve the part of the problem related to the electronic subsystem, ignoring nuclear motion; then, we use the obtained mean distribution of electrons to determine the effective potential of nuclear motion. As a result, we arrive at the well-known Morse curve and Jablonski diagram of vibrational levels [35–37] (see Fig. 9.2). Below, the quantum of the vibrations of molecular nuclei is referred to as a vibron.

Remark 9.1: Phonons The concept of the quasiparticle arises in many-particle problems when properties of a microscopically complex system, such as a semiconductor, may be described as if the system contains various weakly interacting particles.

For example, a charge transfer through a semiconductor or metal is due to the movement of all the electrons interacting with each other and with atomic nuclei. This movement can be represented as the motion of noninteracting electrons with effective masses different from the mass of a free electron traveling in vacuum. Such an electron is called an *electron quasiparticle* [38]. Other examples of quasiparticles are phonons and vibrons.

Phonons are quasiparticles that describe the collective vibrational modes of atoms arranged in a periodic crystal lattice structure. When the atoms vibrate, they create waves of atomic displacements propagating through the lattice. These waves are quantized, and their quanta are called phonons.

(continued)

Remark 9.1 (continued)

Mathematically, phonons are associated with quantized normal modes of the crystal lattice. Each normal mode represents a specific vibrational pattern with a characteristic wave vector $\mathbf{k}$ and frequency $\omega(\mathbf{k})$. Phonons can exhibit different polarizations α, indicating vibrations in different directions relative to the direction of wave vector $\mathbf{k}$.

According to the polarization, phonons can be classified into longitudinal and transverse modes. Longitudinal phonons, which also occur in gases and fluids, involve vibrations where the atoms move parallel to the wave vector $\mathbf{k}$, while transverse phonons occur when the atom vibrations are perpendicular to $\mathbf{k}$.

Since the quantization of phonons can be reduced to the quantization of a quantum oscillator (see Part I), phonons are bosons. As a result of the quantization of transverse phonons, a discrete set of allowed energy bands $E = \hbar\omega(\mathbf{k})$ appears. These bands are often separated by band gaps. In the allowed bands, $\mathbf{k}(\omega)$ is a real vector, while in the band gaps (forbidden bands), $\mathbf{k}(\omega)$ is purely imaginary. The number of the allowed bands is equal to the number of atoms in the elementary cell of the crystal.

For simplest structures with one atom per cell, there is only one band of so-called acoustic phonons. In crystal lattices that contain two or more atoms within an elementary cell, there are additional energy bands of optical phonons with frequencies $\omega(\mathbf{k})$ higher than those in the acoustic band.

A closely related counterpart to the phonon is the vibron. Vibron characterizes a quantized oscillation of the bond connecting atoms in the molecule. The distinction between vibrons and phonons is not always sharply defined, and these terms are frequently used interchangeably.

The adiabatic approximation implies that the Hamiltonian of a molecule can be presented as a sum of the Hamiltonians of electronic and nuclear subsystems, and the eigenenergies of the molecule states as sums of the electronic energies and the quantized energies of nuclear vibrations (horizontal lines in Fig. 9.2). Such an approach implies that there are the eigenstates of a "dressed by vibrons" molecule and that the wave function of such a state can be presented as a product of the wave functions of electrons and vibrating nuclei.

Within the framework of this approximation, Raman scattering received the following explanation. Let us assume that the energy of the state, in which there are neither electronic nor molecular vibronic excitations, is equal to zero (the ground state in Fig. 9.3). It was assumed that a molecule could transition from the ground state to the state with the energy $\hbar\omega_{ext}$ by absorbing a photon with the same energy (this transition is shown by the first blue arrow in Fig. 9.3). Then, the molecule emits a photon with the energy $\hbar\omega_{ext} - \hbar\omega_v$ and transitions to the state with one exited vibron (the green arrow in Fig. 9.3). The emitted photon is the Stokes photon.

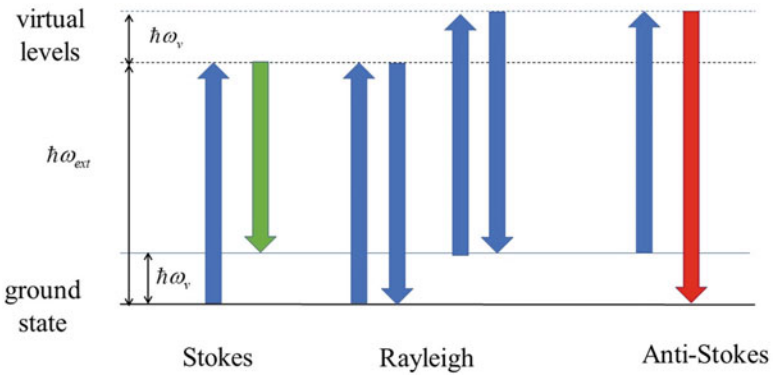

Fig. 9.3 A Jablonski diagram of Raman scattering. The blue arrows correspond to photons having the frequency of the incident photon, the green arrow depicts the emitted photon that excites a vibron, and the red arrow corresponds to the emitted photon that absorbed one vibron

If a molecule initially in the state with one exited vibron absorbs a photon with the energy $\hbar\omega_{ext}$ and transitions back to the ground state (the red arrow in Fig. 9.3), then the radiated photon should have the energy $\hbar\omega_{ext} + \hbar\omega_v$. This is the anti-Stokes photon. Since such a scheme involves two photons (absorbed and emitted), it is called a two-photon scheme.

The population of the state with one excited vibron is less than that of the ground state by the factor $\exp(-\hbar\omega_v/kT)$. The difference in populations is responsible for the difference between Stokes and ant-Stokes intensities.

The fundamental problem, common for Rayleigh and Raman scatterings, has been discussed in Part I. The direct application of the Bohr approach assumes that during the scattering, a photon with a given energy can be absorbed. This requires a resonant level, which is generally absent. Therefore, an additional *virtual* level is usually introduced to satisfy this requirement. This approach is phenomenologically clear, as the transition concept can be described within the Bohr theory. However, the emergence of virtual levels is not founded; their presence is a phenomenological assumption. The second weak point of the approach is that Raman scattering is observed in Raman-active molecules. This means that there is no dipole transition between vibrational levels. All IR transitions are forbidden. Consequently, in the adiabatic theory, the transitions between states with different excited vibration levels are also forbidden.

Raman signals originating from incoherent light sources exhibit inherent weakness. The introduction of lasers, emitting high-intensity coherent light, not only enabled the proportional enhancement of Raman responses with incident light intensity but also unveiled novel coherence-related effects.

The propagation of coherent laser signals through Raman-active media gives rise to the coherent Stokes signal, a phenomenon associated with stimulated Raman scattering (SRS) [39]. Additionally, illuminating Raman-active media with two coherent light beams, featuring a frequency difference equal to the vibron frequency,

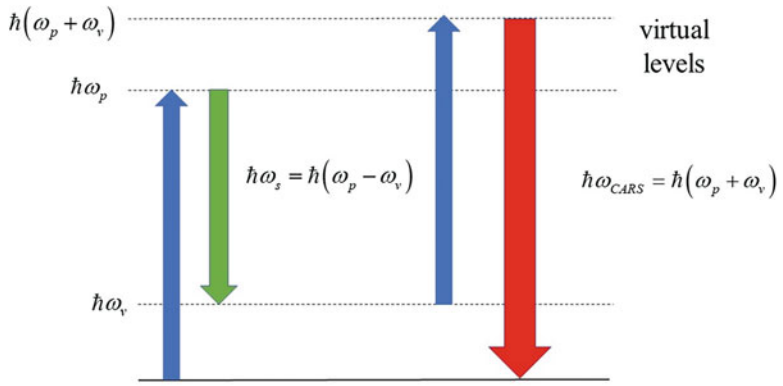

Fig. 9.4 The Jablonski diagram of CARS

gives rise to coherent anti-Stokes Raman scattering (CARS) [40] (see also Refs. [14, 22, 23, 41]). Importantly, CARS exacerbates the challenges posed by the adiabatic theory.

In CARS, one uses two incident beams of coherent light with frequencies ω_p (the pump frequency) and ω_s (the signal frequency). The difference in these frequencies $\omega_p - \omega_s$ equals the eigenfrequency ω_v of the nuclear vibration. To describe CARS, the adiabatic approach requires two more virtual levels [24] (see Fig. 9.4).

The first quantum explanation of CARS was based on the concept of virtual levels. This theory [42] assumes that a photon with the energy $\hbar\omega_p$ excites the molecule from the ground state to the first virtual state. The signal beam of energy $\hbar\omega_s$ stimulates the transition from the first virtual level to the state with the energy $\hbar\omega_v$ (see the diagram in Fig. 9.4), which is the state with one excited vibron. Another photon with the energy $\hbar\omega_p$ is then used to excite the molecule from this state to the second virtual state with the energy $\hbar(\omega_p + \omega_v)$. The spontaneous transition from the latter state returns the molecule to the ground state and results in emitting an anti-Stokes photon. Since four photons are involved in this scheme, it is often called the "four-photon scheme." This consideration suffers from the same shortcomings as the spontaneous Raman scattering explanation. Moreover, the theory says nothing about coherence. It is unclear why, at the spontaneous Raman effect, the transition from virtual levels to ground state results in an incoherent outcome, while in CARS, such a transition makes the response coherent.

High intensity of laser radiation allows us to step back and employ the semiclassical description of a molecule [43, 44], which resorts to the methods of nonlinear optics developed for classical fields, in which the fields are assumed to be coherent [15, 24, 42]. These methods assume that there is a nonlinearity described by susceptibility of the third order $\chi^{(3)}$.

This approach considers that in the CARS scheme, beats of the intensity appear at the frequency $\omega_p - \omega_s$. Due to the parametric interaction of electronic and vibronic subsystems, these beats resonantly excite vibrons in the molecule. Thus, along with

thermal vibrons, coherent vibrons arise. The coherent vibron contributions are responsible for coherent Raman scattering.

In contrast to the spontaneous Raman scattering, in CARS, both Stokes and anti-Stokes components become partially coherent. The main advantage of CARS is that the contribution of the coherent signal is increased as a square of the number N of the illuminated molecules, while incoherent intensity increases linearly. If N is greater than $10^6 - 10^7$, the coherent component prevails. Under the standard conditions, 1 cm^3 of material contains 10^{19} atoms; this number is large enough for the coherent part of the signal to be significant (see Sect. 13.3 for details).

To conclude, neither classical nor the abovementioned quantum approaches provide a consistent description of quantum inelastic scattering. However, considerable theoretical progress has been recently made in studies of the direct interaction between electronic and nuclear degrees of freedom of a molecule [45–48]. It has been understood that the description of the optical inelastic properties of molecules requires an explicit consideration of the interaction between electronic and vibronic degrees of freedom.

An effective approach to solving the problem with a high number of degrees of freedom is to use phenomenological considerations. In particular, when describing complex quantum systems, various types of model Hamiltonians are used. For example, to describe phenomena occurring in complex molecules subjected to external forces, the optical-mechanical Hamiltonian has recently been used [49–51].

In this book, we use the Fröhlich Hamiltonian to study various Raman phenomena. This Hamiltonian is a well-established tool in solid-state physics, particularly in the study of electron-phonon interactions [52–54]. Importantly, recent research has demonstrated the effectiveness of this approach in resolving issues related to Raman scattering [55–57].

In Part I, we consider the forced motion of a quantum system under the influence of an external force; we show that the interaction of a TLS with a single light mode results in driven oscillation of the TLS dipole moment with the frequency of the external field. Such a driven response is modulated with an off-resonant Rabi frequency.

In this part, we generalize the approach developed for considering the modulation of the Rayleigh scattering by the frequency of intramolecular oscillations. We employ the Fröhlich Hamiltonian to analyze various effects of Raman scattering, such as coherent anti-Stokes Raman scattering (CARS), surface-enhanced Raman scattering (SERS), stimulated Raman scattering (SRS), and Raman lasing [49, 56]. Special attention is paid to the coherence of the emitted light. We consider the first-order coherence usually associated with obtaining interference fringes when two fields are superimposed.

In Chap. 10, we derive the Hamiltonian that governs the interaction between photons and vibrons in a molecule, focusing on its application in the context of Raman scattering. To simplify our analysis, we employ a hydrogen molecule as a model system. The extension of the derivation to more complex molecules, while technically intricate, remains conceptually straightforward. Our investigation centers around the utilization of the Fröhlich Hamiltonian to explore various Raman phenomena.

Chapter 11 focuses on spontaneous Raman scattering. Building upon the molecular Hamiltonian established in the preceding chapter, we introduce an additional term accounting for the interaction between the electronic subsystem and an external electromagnetic field. We also consider the interactions of both the electronic and vibronic subsystems with reservoirs.

Employing the Born-Markov approximation, we effectively eliminate operators associated with the reservoirs' degrees of freedom, enabling the derivation of the Heisenberg-Langevin equations for all pertinent operators. To address this complex system of nonlinear operator equations, we develop a perturbation theory. This approach provides us with the necessary tools to describe the Raman effect within this framework.

In Chap. 12, we explore surface-enhanced Raman scattering (SERS), a highly effective technique for amplifying Raman signals. This phenomenon stems from the localized enhancement of the scattered field, driven by plasmonic resonance.

Within this chapter, we elucidate the fundamental mechanisms behind the amplification of Raman signals. Two critical factors come into play: first, the intensification of the incident electric field's strength, due to plasmonic resonance, and the augmentation of radiated intensity, driven by the Purcell effect.

In Chap. 13, we study the phenomenon where a Raman-active molecule is illuminated by two coherent waves, specifically the pumping and signal waves. The interaction between the pump wave and the molecule leads to the transfer of energy to the signal wave. This outcome is described by using nonlinear optics, utilizing the third-order nonlinear susceptibility. In the literature, this effect is commonly referred to as Raman amplification.

Additionally, this chapter delves into the realm of coherent anti-Stokes Raman scattering (CARS) from both quantum and semiclassical perspectives. We determine the amplitude of the CARS signal and analyze the conditions that foster amplification.

Chapter 14 delves into the manifestation of the Raman effect within conventional lasers. We demonstrate that when the interaction constant between the electronic and vibronic subsystems surpasses a critical value, a second lasing threshold emerges. Above this threshold, the laser spectrum undergoes a transformation, featuring distinct characteristic frequencies shifted from the conventional laser frequencies. Additionally, the interplay with other parameters leads to the prediction of diverse lasing regimes, including the possibility of a chaotic regime.

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Chapter 10
The Hamiltonian of the Interaction Between Electronic and Nuclear Subsystems of a Molecule

In this chapter, we derive the Hamiltonian of the light-molecule interaction that describes Raman scattering. For simplicity, we consider a hydrogen molecule. The generalization to more complex molecules is technically more complicated but conceptually straightforward.

Our immediate goal is to find a mechanism leading to Raman scattering of light on molecules. We show that in a Raman-active molecule, light directly interacts only with electrons, not nuclei. Unlike Rayleigh scattering, Raman scattering is inelastic, and the electronic subsystem of a molecule radiates at two additional frequencies along with the frequency of incident light. The Raman frequency shifts are independent of the frequency of the incident light and are determined by the natural frequency of vibrations of molecular nuclei. This indicates that the system Hamiltonian should include the interaction between oscillations of the electronic subsystem and nuclear vibration.

A hydrogen molecule consists of two nuclei and two electrons. In the reference frame, whose origin is at the center of mass of nuclei, in nonrelativistic approximation, the system is described by the Hamiltonian:

$$\widehat{H} = \sum_{i=1,2} \left[\frac{\mathbf{p}_i^2}{2m} - \frac{e^2}{|\mathbf{r}_i + \mathbf{R}/2|} - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}/2|} + \mathbf{E}(t) \cdot e\mathbf{r}_i \right] + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{\mathbf{P}^2}{2M} + \frac{e^2}{R} \tag{10.1.1}$$

where R is the distance between the nuclei; $\mathbf{p}_i$ and $\mathbf{r}_i$ are the momentum and the position of the ith electron, respectively; $\mathbf{P}$ is the total momentum of the nuclei; $\pm\mathbf{R}/2 = \pm\,\mathbf{n}R/2$ are the position vectors of the nuclei (Fig. 10.1); $\mathbf{n}$ is a unit vector pointing along the molecule; M is the reduced mass of the nuclei; e is an electron charge; and $\mathbf{E}(t)$ is the external electric field. The sum in parentheses of Eq. (10.1.1) includes the kinetic energy of electrons and the energies of their interaction with protons and the external electric field. The term $e^2/|\mathbf{r}_1 - \mathbf{r}_2|$ is Coulomb's interaction

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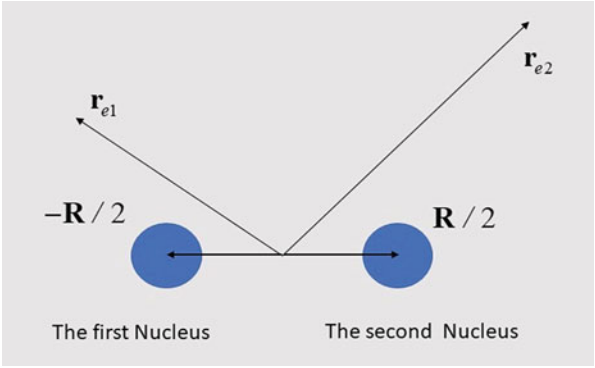

Fig. 10.1 Schematics of a hydrogen molecule. The origin of the reference frame is in the center of mass of the molecule. $\mathbf{r}_{e1}$ and $\mathbf{r}_{e2}$ coordinates of electrons, and $(-\mathbf{R}/2)$ and $\mathbf{R}/2$ are coordinates of nuclei

energy of electrons with each other. The last two terms of Hamiltonian (10.1.1) are the kinetic energy of the relative motion of the nuclei and the potential energy of their interaction, respectively.

A part of Hamiltonian (10.1.1)

$$U(\mathbf{r}_{e1}, \mathbf{r}_{t2}, \mathbf{R}) = -\frac{e^2}{|\mathbf{r}_{e1} + \mathbf{R}/2|} - \frac{e^2}{|\mathbf{r}_{e1} - \mathbf{Rn}/2|} - \frac{e^2}{|\mathbf{r}_{e2} + \mathbf{R}/2|} - \frac{e^2}{|\mathbf{r}_{e2} - \mathbf{R}/2|} + \frac{e^2}{R} \tag{10.1.2}$$

is the total energy of Coulomb's interaction of all involved charges.

As we discussed in the Introduction, one can use the Born-Oppenheimer approximation and consider the motion of electrons and nuclei separately using different Schrödinger equations. This approximation implies that the sum of the Hamiltonians of these equations is the Hamiltonian of the molecule. Consequently, the wave function of a molecule is a product of the wave functions of the electron and nuclear subsystems. The price for such a simplification is that when calculating the state of the electronic system, we do not account for the quantum nature of nuclei, fixing their locations and ignoring the fact that the nuclei are in fixed positions only with some probability. After such a simplification, the Hamiltonian of the electronic subsystem looks as

$$\widehat{H}_{el} = \frac{\widehat{\mathbf{p}}_1^2}{2m} + \frac{\widehat{\mathbf{p}}_2^2}{2m} + e(\mathbf{r}_{e1} + \mathbf{r}_{e2}) \cdot \mathbf{E}_{ext} + U(\mathbf{r}_{e1}, \mathbf{r}_{e2}, R). \tag{10.1.3}$$

Now, we can find the eigenenergies of the electronic subsystem $\{E_a(\widetilde{R})\}$ and corresponding wave functions $\varphi_a(\mathbf{r}_{e1}, \mathbf{r}_{e2}; \widetilde{R})$ by assuming the distance between the nuclei R is fixed $R = \widetilde{R}$ [1]. In this case, as long as we do not consider variations of R, we can disregard the direct Coulomb interaction between nuclei e^2/R. The approaches to solving this problem are well-developed [2]. For the ground state, the obtained dependence of eigenenergy $E_g(R)$ is qualitatively shown in Fig. 9.2. Usually, it is approximated with the Morse curve [3].

Using the obtained wave function $\varphi_a(\mathbf{r}_1, \mathbf{r}_2; \widetilde{R})$ as an electronic wave function, which is a part of the adiabatic wave function of the molecule, $\varphi_a(\mathbf{r}_1, \mathbf{r}_2; \widetilde{R})\chi_a(R)$, turns the rest of the Schrödinger equation with Hamiltonian (10.1.1) into the Schrödinger equation for the wave function of nuclei:

$$\left(\frac{\widehat{\mathbf{P}}^2}{2M} + E_a(R)\right)\chi_a(R) = \varepsilon_a\chi_a(R). \tag{10.1.4}$$

We can see that not U but $E_a(R)$ plays the role of the effective potential for nuclear motion. This is important because unlike the electrostatic potential U, which, according to Earnshaw's theorem [4], cannot have a minimum, $E_a(R)$ has a minimum determined by the equation $\partial E_a(R)/\partial R = 0$. We denote the position of the minimum by R_0. The presence of such a minimum leads to the stability of the hydrogen molecule, which is a quantum mechanical effect. Comparing the values of the energy levels of the molecule obtained by the theory and experiment, we can see that those results are in good agreement [5].

Unfortunately, with this approach, the Hamiltonian of the interaction between electronic and nucleus subsystems disappears.

If we want to take into account the influence of nucleus motion on the electronic subsystem, then we cannot split the Schrödinger equation for the molecular wave function into two independent equations. The operator of the nucleus kinetic energy $\widehat{\mathbf{P}}^2/(2M)$ affects the electronic wave functions $\varphi_a(\mathbf{r}_{e1}, \mathbf{r}_{e2}; R)$[1] because $\widetilde{R}$ is no longer a constant. The eigenenergy $E_a(R)$ and, consequently, the Morse potential become time-dependent.

Indeed, by multiplying the Schrödinger equation by $\varphi_b^*(\mathbf{r}_{e1}, \mathbf{r}_{e2}; R)$ and integrating over the electronic coordinates, we obtain:

$$\begin{aligned}
&\int d\mathbf{r}_{e1}d\mathbf{r}_{t2}\varphi_b^*(\mathbf{r}_{e1}, \mathbf{r}_{t2}; R)\widehat{H}\varphi_a(\mathbf{r}_{e1}, \mathbf{r}_{t2}; R)\chi_a(R) \\
&= \int d\mathbf{r}_{e1}d\mathbf{r}_{t2}\varphi_b^*(\mathbf{r}_{e1}, \mathbf{r}_{e2}; R)\left(\widehat{H}_{el}(r, R) + \frac{\widehat{\mathbf{P}}^2}{2M}\right)\varphi_a(\mathbf{r}_{e1}, \mathbf{r}_{e2}; R)\chi_a(R) \\
&= \int d\mathbf{r}_{e1}d\mathbf{r}_{t2}\varphi_b^*(\mathbf{r}_{e1}, \mathbf{r}_{e2}; R)\widehat{H}_{el}(r, R)\varphi_a(\mathbf{r}_{e1}, \mathbf{r}_{e2}; R)\chi_a(R) \\
&\quad + \int dr\varphi_b(r; R)\frac{\widehat{\mathbf{P}}^2}{2M}\varphi_a(r; R)\chi_a(R) \\
&= E_a(R)\delta_{ab}\chi_a(R) + \int d\mathbf{r}_{e1}d\mathbf{r}_{t2}\varphi_b^*(\mathbf{r}_{e1}, \mathbf{r}_{e2}; R)\frac{\mathbf{P}^2}{2M}\varphi_a(\mathbf{r}_{e1}, \mathbf{r}_{e2}; R)\chi_a(R) \\
&= \varepsilon_a\delta_{ab}\chi_a(R)
\end{aligned}$$

or

[1] The presence of an external optical field significantly complicates the problem. Now we must also take into account the fact that the electronic wave function oscillates with optical frequencies.

$$(E_a(R)-\varepsilon_{ab})\delta_{ab}\chi_a(R).$$
$$= -\int d\mathbf{r}_{e1}d\mathbf{r}_{t2}\varphi_b^*(\mathbf{r}_{e1},\mathbf{r}_{e2};R)\frac{\mathbf{P}^2}{2M}\varphi_a(\mathbf{r}_{e1},\mathbf{r}_{t2};R)\chi_a(R) \equiv \sum_b \widehat{h}_{ab}^{(non-ad)}\chi_b(R). \tag{10.1.5}$$

In the general case, nuclear wave functions are coupled to each other, and each of them depends on all electronic configurations. The coupling operator $\widehat{h}_{ab}^{(non-ad)}$ is referred to as a non-adiabaticity operator.

This means that one cannot describe the interaction between electron and nucleus subsystems in the adiabatic approximation. To find the interaction operator, we should come back and analyze Hamiltonian (10.1.1).

Below, we take into account that, firstly, the nuclei can move along only one direction; consequently, the coordinate and momentum of nuclei are scalar operators $\widehat{R}$ and $\widehat{P}$, and, secondly, that the nuclei still oscillate in the vicinity of the minimum of the Morse curve and we can expand the potential U in Taylor's series in terms of $\delta R_0/R_0$:

$$\widehat{H} = \frac{\widehat{\mathbf{p}}_1^2}{2m}+\frac{\widehat{\mathbf{p}}_2^2}{2m}+U(r,R_0)\widehat{I}+\mathbf{P}^2/2M+e(\mathbf{r}_{e1}+\mathbf{r}_{e2})\cdot\mathbf{E}_{ext}\widehat{I} \tag{10.1.6}$$
$$+\left[\left(\frac{\partial U(r,R)}{\partial R}\right)\Bigg|_{R=R_0}\delta\widehat{R}+\frac{1}{2}\left(\frac{\partial^2 U(r,R)}{\partial R^2}\right)\Bigg|R=R_0\left(\delta\widehat{R}\right)^2\right]\widehat{I},$$

where R_0 is the position of the minimum of $E_a(R)$.

Below, we also assume that in all scattering processes, the only two lowest levels of the electronic subsystem play a significant role, and the probabilities of excitations of higher electronic levels are so small that they can be neglected (i.e., the molecule is treated as a TLS). Thus, we restrict ourselves to considering only two electronic states $\varphi_g(r;R_0)=|g\rangle(R_0)$ and $\varphi_e(r;R_0)=|e\rangle(R_0)$. The energies of these states are separated by the energy $\hbar\omega_\sigma(R_0)$.

The next step is relating the parameters of the TLS to the ones of Hamiltonian (10.1.6). The wave functions $\varphi_g(r;R_0)=|g\rangle(R_0)$ and $\varphi_e(r;R_0)=|e\rangle(R_0)$ are determined by the first three terms of Eq. (10.1.6). Assuming that the energy of the ground state of the electron subsystem equals zero, we can write these three terms in a simple form (see Sect. 2):

$$\widehat{H}_{TLS}=\hbar\omega_\sigma(R_0)\widehat{\sigma}^\dagger\widehat{\sigma}. \tag{10.1.7}$$

The term

$$e(\mathbf{r}_{e1}+\mathbf{r}_{e2})\cdot\mathbf{E} \tag{10.1.8}$$

is proportional to the dipole moment of the molecule. This term can be written as the operator of the interaction of the molecule with the external field as

$$-\left(\mathbf{E}(t)\cdot\widehat{\mathbf{d}}\right)/\hbar$$

where $\widehat{\mathbf{d}}=\mathbf{d}_{eg}\left(\widehat{\sigma}^{\dagger}+\widehat{\sigma}\right)$ is the Hermitian operator of the dipole moment of the electronic subsystem (see Sect. 2.2). For the external harmonic field $\mathbf{E}_{ext}\cos(\omega_{ext}t)$, one can introduce the coupling constant (the Rabi frequency),

$$\Omega_{ext}=-\left(\mathbf{E}_{ext}\cdot\mathbf{d}_{\mathrm{eg}}\right)/\hbar,$$

and using the rotating wave approximation (see Sect. 2.4), rewrite term (10.1.8) as $\hbar\Omega(t)\left(\widehat{\sigma}^{\dagger}+\widehat{\sigma}\right)/2$. Finally, we arrive at the following expression:

$$-\left(\mathbf{E}(t)\cdot\widehat{\mathbf{d}}\right)/\hbar=\hbar\Omega_{ext}\left(\widehat{\sigma}_H^{\dagger}\exp(-i\omega_{ext}t)+\widehat{\sigma}_H\exp(i\omega_{ext}t)\right)/2 \tag{10.1.9}$$

Taking into account that the Hilbert space of the wave function of the electronic subsystem is two-dimensional, we can express the operators acting on the functions as

$$\begin{aligned}U&=U_{11}|e\rangle\langle e|+U_{12}|e\rangle\langle g|+U_{21}|g\rangle\langle e|+U_{22}|g\rangle\langle g|\\&=U_{11}\sigma^{\dagger}\sigma+U_{12}\sigma^{\dagger}+U_{21}\sigma+U_{22}\left(\widehat{I}-\sigma^{\dagger}\sigma\right)=(U_{11}-U_{22})\sigma^{\dagger}\sigma+U_{12}\sigma^{\dagger}+U_{21}\sigma+U_{22}\widehat{I}\end{aligned}$$

where $|e\rangle\langle e|=\sigma^{\dagger}\sigma$, $|e\rangle\langle g|=\sigma^{\dagger}$, $|g\rangle\langle e|=\sigma$, $|g\rangle\langle g|=I-|e\rangle\langle e|=I-\sigma^{\dagger}\sigma$. Then, two terms in square brackets of Hamiltonian (10.1.6) can be written in the TLS basis as

$$\begin{aligned}&\left[\left(\frac{\partial U(R)}{\partial R}\right)|R=R_0\delta R+\frac{1}{2}\left(\frac{\partial^2U}{\partial R_i\partial R_j}\right)_{R=R_0}(\delta R)^2\right]\widehat{I}\\&\quad=\delta R\Bigg(\langle e|\left(\frac{\partial U(R)}{\partial R}\right)\Big|_{R=R_0}|e\rangle\widehat{\sigma}^{\dagger}\widehat{\sigma}+\langle g|\left(\frac{\partial U(R)}{\partial R}\right)\Big|_{R=R_0}|g\rangle\left(\widehat{I}-\widehat{\sigma}^{\dagger}\widehat{\sigma}\right)\\&\qquad+\langle e|\left(\frac{\partial U(R)}{\partial R}\right)\Big|_{R=R_0}|g\rangle\widehat{\sigma}^{\dagger}+\langle g|\left(\frac{\partial U(R)}{\partial R}\right)\Big|_{R=R_0}|e\rangle\widehat{\sigma}\Bigg)\\&\qquad+\frac{(\delta R)^2}{2}[\Bigg(\langle g|\left(\frac{\partial^2U(R)}{\partial R^2}\right)|_{R=R_0}|g\rangle\\&\qquad+\langle e|\left(\frac{\partial^2U(R)}{\partial R^2}\right)\Big|_{R=R_0}|e\rangle-2\langle g|\left(\frac{\partial^2U(R)}{\partial R^2}\right)\Big|_{R=R_0}|g\rangle\Bigg)\widehat{\sigma}^{\dagger}\widehat{\sigma}\\&\qquad+\langle e|\left(\frac{\partial^2U(R)}{\partial R^2}\right)\Big|_{R=R_0}|g\rangle\widehat{\sigma}^{\dagger}+\langle g|\left(\frac{\partial^2U(R)}{\partial R^2}\right)\Big|_{R=R_0}|e\rangle\widehat{\sigma}],\end{aligned} \tag{10.1.10}$$

The characteristic frequencies of oscillations of molecular nuclei are in the range of $0.01-0.1\,\mathrm{eV}$, while the characteristic frequencies of transitions in the electronic

subsystem are much higher, $1-10\,\mathrm{eV}$. Taking into account that $\delta R/R_0 \ll 1$, we can neglect the term:

$$\delta R^2\left(\langle e|\left(\frac{\partial^2 U(R)(R)}{\partial R^2}\right)|_{R=R_0}|e\rangle - 2\langle g|\left(\frac{\partial^2 U(R)(R)}{\partial R^2}\right)|_{R=R_0}|g\rangle\right)\widehat{\sigma}^{\dagger}\widehat{\sigma}/2 \quad (10.1.11)$$

compared to the term $\delta R\langle e|\frac{\partial U(R)}{\partial R_0}|e\rangle\widehat{\sigma}^{\dagger}\widehat{\sigma}$.

Also, under the influence of the monochromatic external field, the operator $\widehat{\sigma}$ oscillates with the frequency of the external field ω_{ext}, while the operator $\widehat{\sigma}^{\dagger}\widehat{\sigma}$ varies slowly in comparison with $\widehat{\sigma}$ (see Eqs. (2.4.19)-(2.4.20)). Therefore, in Eq. (10.1.10), the terms $\langle e|\left(\frac{\partial U(R)}{\partial R}\right)|_{R=R_0}|g\rangle\widehat{\sigma}^{\dagger}$ and $\langle g|\left(\frac{\partial U(R)}{\partial R}\right)|_{R=R_0}|e\rangle\widehat{\sigma}$ oscillate much faster than the terms $\langle e|\left(\frac{\partial U(R)}{\partial R}\right)|_{R=R_0}|e\rangle\widehat{\sigma}^{\dagger}\widehat{\sigma}$ and $\langle g|\left(\frac{\partial U(R)}{\partial R}\right)|_{R=R_0}|g\rangle\left(\widehat{I}-\widehat{\sigma}^{\dagger}\widehat{\sigma}\right)$. Considering that in the rotating wave approximation (see Eq. (10.1.9)), Hamiltonian (10.1.6) contains only slowly varying terms, without exceeding the accuracy of reasoning, we should neglect the rapidly oscillating terms $\langle e|\left(\frac{\partial^2 U(R)}{\partial R^2}\right)|_{R=R_0}|g\rangle\widehat{\sigma}^{\dagger}$ and $\langle g|\left(\frac{\partial^2 U(R)}{\partial R^2}\right)|_{R=R_0}|e\rangle\widehat{\sigma}$.

After such simplifications, Hamiltonian (10.1.6) takes the form:

$$\begin{aligned}\widehat{H} &= \hbar\omega_{\sigma}(R_0)\widehat{\sigma}^{\dagger}\widehat{\sigma} + \hbar\Omega_{ext}\left(\widehat{\sigma}_H^{\dagger}\exp(-i\omega_{ext}t) + \widehat{\sigma}_H\exp(i\omega_{ext}t)\right)/2 + \mathbf{P}^2/2M \\ &+\langle e|\left(\frac{\partial U(R)}{\partial R}\right)|_{R=R_0}|e\rangle\delta\widehat{R}\widehat{\sigma}^{\dagger}\widehat{\sigma} + \frac{1}{2}\langle g|\left(\frac{\partial^2 U(R)}{\partial R^2}\right)|_{R=R_0}|g\rangle\left(\delta\widehat{R}\right)^2\widehat{I}.\end{aligned} \quad (10.1.12)$$

The Hamiltonian of the nuclear subsystem is represented by the terms:

$$\widehat{H}_{nucl} = \frac{\mathbf{P}^2}{2M} + \frac{1}{2}\langle g|\left(\frac{\partial^2 U(R)}{\partial R^2}\right)|_{R=R_0}|g\rangle\delta R^2 \quad (10.1.13)$$

This is a Hamiltonian of a classical oscillator

$$\widehat{H}_{cl\,os}(\delta R) = \frac{\mathbf{P}^2}{2M} + \frac{M\omega_v^2}{2}\delta R^2$$

with

$$\omega_{\mathrm{v}} = \sqrt{\langle g|\left(\frac{\partial^2 U(R)}{\partial R^2}\right)|_{R=R_0}|g\rangle/M} \quad (10.1.14)$$

Note that the eigenfrequency ω_{v} may differ from the eigenfrequency $\varepsilon_a/\hbar$ of Eq. (10.1.4) obtained with the assumption that $\widehat{h}_a^{(non-ad)} = 0$.

From Eq. (10.1.14), using $U \sim \hbar\omega_\sigma$ and that the characteristic distance between molecular nuclei is Bohr radius a, the vibration eigenfrequency can be evaluated as follows:

$$\omega_\nu \sim \sqrt{\hbar\omega_\sigma / a^2 M} \sim \omega_\sigma \sqrt{\hbar / a^2 \omega_\sigma M} \sim \omega_\sigma \sqrt{m/M} \tag{10.1.15}$$

where at the last step we exploit that for hydrogen-like molecules $\omega_\sigma \sim me^4/\hbar^3$ and $a \sim \hbar^2/me^2$, m is an effective electron mass.

Finally, we quantize the Hamiltonian $\widehat{H}_{nucl}$ (Eq. (10.1.13)). To do this, we should consider the nuclear displacement as the operator $\delta\widehat{R}$ (see Sect. 2.5.1). Then, $\widehat{H}_{nucl}$ becomes the Hamiltonian of a quantum oscillator, and we can introduce operators $\widehat{b}^+$ and $\widehat{b}$ for the creation and annihilation of the excitations of nuclear oscillations that satisfy the boson commutation relation $\left[\widehat{b}, \widehat{b}^\dagger\right] = \widehat{1}$. The operator $\delta\widehat{R}$ and operators $\widehat{b}^\dagger$ and $\widehat{b}$ are connected through the equality:

$$\delta\widehat{R} = \sqrt{\frac{\hbar}{2M\omega_\nu}}\left(\widehat{b}^+ + \widehat{b}\right) \tag{10.1.16}$$

In terms of these operators, Hamiltonian (10.1.13) takes the form:

$$\widehat{H}_{\text{nucl}} = \hbar\omega_\nu \widehat{b}^+ \widehat{b} \tag{10.1.17}$$

The last two terms of Hamiltonian (10.1.12) can be written as

$$\begin{aligned}\left(\langle e|\left(\frac{\partial U(R)}{\partial R}\right)|_{R=R_0}|e\rangle - \langle g|\left(\frac{\partial U(R)}{\partial R}\right)|_{R=R_0}|g\rangle\right)\delta R\widehat{\sigma}^\dagger\widehat{\sigma} \\ = \left(\langle e|\left(\frac{\partial U(R)}{\partial R}\right)|_{R=R_0}|e\rangle - \langle g|\left(\frac{\partial U(R)}{\partial R}\right)|_{R=R_0}|g\rangle\right)\sqrt{\frac{\hbar}{2M\omega_\nu}}\left(\widehat{b}^+ + \widehat{b}\right)\widehat{\sigma}^\dagger\widehat{\sigma},\end{aligned} \tag{10.1.18}$$

These terms are responsible for the interaction of electrons and vibrations of the molecule nuclei.

It is worth emphasizing that in various electronic states, eigenenergy minima are achieved at different arrangements of the nuclei. Thus, a harmonic external field, causing the Rabi oscillations of the electronic subsystem, should affect the nuclei system, causing the nuclear subsystem to move between positions having $R_0(|g\rangle)$ and $R_0(|e\rangle)$. This fact is reflected in Eq. (10.1.18), and vice versa, the nuclear vibration modulates the dipole moment of the electronic subsystem.

Below, we denote the interaction constant between the TLS and nuclear vibrations as

$$g = \left(\langle e| \left(\frac{\partial U(R)}{\partial R} \right) |_{R=R_0} |e\rangle - \langle g| \left(\frac{\partial U(R)}{\partial R} \right) |_{R=R_0} |g\rangle \right) \sqrt{\frac{1}{2M\hbar\omega_v}}, \tag{10.1.19}$$

so that Eq. (10.1.18) becomes:

$$\hbar g \left(\hat{b}^+ + \hat{b} \right) \hat{\sigma}^\dagger \hat{\sigma}. \tag{10.1.20}$$

From Eq. (10.1.19), the constant g can be evaluated as follows:

$$g \sim \frac{\hbar\omega_\sigma}{a} \sqrt{\frac{1}{M\hbar\omega_v}} \sim \omega_\sigma (m/M)^{1/4}, \tag{10.1.21}$$

From Eqs. (10.1.15) and (10.1.21), we have:

$$g/\omega_v \sim (m/M)^{1/4} \leq 1, \tag{10.1.22}$$

For real substances, the ratio g/ω_v can vary in a wide range from 10^{-1} to 10 [6, 7].

Hamiltonian (10.1.20) has the form of commonly used in solid-state physics Fröhlich Hamiltonian that describes the electron-phonon interaction (see, e.g., Refs. [8–10]). This Hamiltonian is of the dephasing type (see Sect. 3.2.3).

Finally, combining Eqs. (10.1.13)–(10.1.18), we obtain the complete quantized Hamiltonian of a molecule interacting with an EM field:

$$\hat{H} = \hbar\omega_0 \hat{\sigma}^\dagger \hat{\sigma} + \hbar\omega_v \hat{b}^+ \hat{b} + \hbar\Omega_{ext} \left(\hat{\sigma}^\dagger \exp(-i\omega_{ext} t) + \hat{\sigma} \exp(i\omega_{ext} t) \right)/2 + \hbar g \left(\hat{b}^+ + \hat{b} \right) \hat{\sigma}^\dagger \hat{\sigma} \tag{10.1.23}$$

To clarify the parametric nature of the effect of nuclear vibrations on the radiation frequency of the electron system, we combine the first and last terms of Hamiltonian (10.1.23):

$$\hbar\omega_\sigma \hat{\sigma}^\dagger \hat{\sigma} + \hbar g \hat{\sigma}^\dagger \hat{\sigma} \left(\hat{b}^\dagger + \hat{b} \right) = \hbar \left[\omega_\sigma + g \left(\hat{b}^\dagger + \hat{b} \right) \right] \hat{\sigma}^\dagger \hat{\sigma}$$

From this expression, one can see that the displacement $\left\langle \delta\hat{R} \right\rangle \sim \left\langle \left(\hat{b}^+ + \hat{b} \right) \right\rangle \neq 0$ of a nucleus from the equilibrium position results in a change in the transition frequency ω_σ of the electronic subsystem of the molecule. That is, the movement of nuclei about their equilibrium positions leads to a modulation of the transition frequency of the effective TLS. For this reason, the considered interaction is often called parametric. As we see below, the described interaction mechanism leads to the Raman effect. Such a simple interpretation, of course, gives only qualitative results.

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Chapter 11
Spontaneous Raman Scattering

As Hamiltonian (10.1.23) describing the electron-vibron interaction has been introduced, we can consider Raman scattering of a monochromatic wave incident on a molecule.

In addition to the external field, the electronic subsystem may interact with reservoirs responsible for relaxation processes in the molecule. These are the reservoir of the free space modes (see Eq. (11.1.2) and, Sect. 3.1) and the dephasing reservoir arising due to the impact broadening of atoms' spectral lines in gases or other elastic interactions with the surrounding medium [see Eqs. (3.2.51)–(3.2.52)]. The vibrational modes of the nuclear subsystem interact with the thermal reservoir of the environment [1]. The model Hamiltonian describing these reservoirs has the form:

$$\widehat{H}_R = \sum_{\mathbf{k},\,\mu} \hbar\omega_{\mathbf{k}} \widehat{a}^{\dagger}_{\mathbf{k},\mu} \widehat{a}_{\mathbf{k},\mu} + \sum_{n} \hbar\omega_n^{dp} \widehat{c}_n^{\mathrm{dp}\dagger} \widehat{c}_n^{dp} + \sum_{l} \hbar\omega_l^{m} \widehat{c}_l^{\mathrm{m}\dagger} \widehat{c}_l^{m}. \tag{11.1.1}$$

In this Hamiltonian, the first term describes the reservoir of free space EM modes. Operators $\widehat{a}^{\dagger}_{\mathbf{k},\mu}$ and $\widehat{a}_{\mathbf{k},\mu}$ are creation and annihilation operators of the photon with the wave vector $\mathbf{k}$ and the polarization, μ. The second term corresponds to the dephasing reservoir of an elastic interaction with, say, atomic vibrations in the environment. The latter are quantized and described by the creation and annihilation operators $\widehat{c}_n^{dp\dagger}$ and $\widehat{c}_n^{dp}$. The third term represents the reservoir responsible for the relaxation of the vibron modes of the molecule [2–5].

In the rotating wave approximation (see Eq. (2.4.6)), which is used throughout this part, the interaction of the system with the reservoirs is described by the Hamiltonian:

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$$\begin{aligned}\widehat{H}_{SR} = &\sum_{\mathbf{k},\mu} \mathbf{E}_{\mathbf{k},\mu} \cdot \mathbf{d}_{\mathrm{eg}} \left(\widehat{\sigma} \widehat{a}^{\dagger}_{\mathbf{k},\mu} + \widehat{\sigma}^{\dagger} \widehat{a}_{\mathbf{k},\mu} \right) \\ &+ \sum_{n} \hbar \kappa_n^{dp} \left(\widehat{c}_n^{dp\dagger} + \widehat{c}_n^{dp} \right) \widehat{\sigma}^{\dagger} \widehat{\sigma} + \sum_{l} \hbar \kappa_l^{mol} \left(\widehat{c}_l^{mol\dagger} \widehat{b} + \widehat{c}_l^{mol} \widehat{b}^{\dagger} \right)\end{aligned} \tag{11.1.2}$$

The first term in interaction Hamiltonian (11.1.2) is similar to the one in Hamiltonian (10.1.9), in which the external field is replaced by the quantized field of the free space mode with the wave vector $\mathbf{k}$ and the polarization μ. In this term, $\mathbf{E}_{\mathbf{k},\,\mu}$ is the electric field per one photon. We assume that this Hamiltonian is of the Jaynes-Cummings type. The quantity κ_n^{dp} is the interaction constant of the electronic subsystem with the n-th mode of the dephasing reservoir, which is assumed to be of the Fröhlich type. The quantities κ_l^{mol} are the interaction constants of the vibronic modes of the molecule with the thermal reservoir of the environment.

The Hamiltonian of the total system is the sum of Hamiltonians (10.1.23), (11.1.1), and (11.1.2):

$$\begin{aligned}\widehat{H} = &\hbar\omega_0 \widehat{\sigma}^{\dagger}\widehat{\sigma} + \hbar\omega_{\mathrm{v}} \widehat{b}^{+}\widehat{b} + \hbar \frac{\Omega_{ext}}{2} \left(\widehat{\sigma}^{\dagger} e^{-i\omega_{ext}t} + \widehat{\sigma} e^{i\omega_{ext}t} \right) + \hbar g \left(\widehat{b}^{+} + \widehat{b} \right) \widehat{\sigma}^{\dagger}\widehat{\sigma} \\ &+ \sum_{\mathbf{k},\mu} \mathbf{E}_{\mathbf{k},\mu} \cdot \mathbf{d}_{\mathrm{eg}} \left(\widehat{\sigma}^{\dagger} \widehat{a}_{\mathbf{k},\mu} + \widehat{\sigma} \widehat{a}^{\dagger}_{\mathbf{k},\mu} \right) \\ &+ \sum_{\mathbf{k},\mu} \hbar\omega_{\mathbf{k}} \widehat{a}^{\dagger}_{\mathbf{k},\mu} \widehat{a}_{\mathbf{k},\mu} + \sum_{n} \hbar\omega_n^{dp} \widehat{c}_n^{\mathrm{dp}\dagger} \widehat{c}_n^{dp} + \sum_{l} \hbar\omega_l^{m} \widehat{c}_l^{\mathrm{m}\dagger} \widehat{c}_l^{m} \\ &+ \sum_{n} \hbar \kappa_n^{dp} \left(\widehat{c}_n^{dp\dagger} + \widehat{c}_n^{dp} \right) \widehat{\sigma}^{\dagger}\widehat{\sigma} + \sum_{l} \hbar \kappa_l^{mol} \left(\widehat{c}_l^{mol\dagger} \widehat{b} + \widehat{c}_l^{mol} \widehat{b}^{\dagger} \right)\end{aligned} \tag{11.1.3}$$

The next step is to derive the Heisenberg equations for all unknown operators. Comparing the Rabi Hamiltonian (Eq. (2.4.1)) to Hamiltonian (10.1.23), we can see that the former has two additional terms $\hbar\omega_{\mathrm{v}} \widehat{b}^{+}\widehat{b} + \hbar g \left(\widehat{b}^{+} + \widehat{b} \right) \widehat{\sigma}^{\dagger}\widehat{\sigma}$ connected with nuclear vibrations. Following Problem 1.2, one can see that due to this difference, the additional term $-ig\widehat{\sigma}\left(\widehat{b}^{\dagger} + \widehat{b} \right)$ in the equation for $\widehat{\sigma}$ and the term $-ig\widehat{\sigma}^{\dagger}\widehat{\sigma}$ in the equation for $\widehat{b}$ arise (see Eqs. (11.1.4) and (11.1.5)).

Using the Born-Markov approximation (Remark 3.1), one can eliminate the operators corresponding to the reservoirs' degrees of freedom. This can be done when the reservoirs are in thermal equilibrium at a fixed temperature and the interaction of the system with the reservoir is weak. This procedure results in the emergence of dissipation and noise terms in the Heisenberg equations. In the rotating wave approximation, one can obtain the following Heisenberg-Langevin equations (see Problems 1.2 and 1.6, in Part I) for the TLS transition operator $\widehat{\sigma}$ and the operator of the vibration amplitude of the molecule nuclear $\widehat{b}$:[1]

[1] The operators $\widehat{\sigma}^{\dagger}$ and $\widehat{b}^{\dagger}$ are governed by corresponding complex conjugated equations.

$$\frac{d\widehat{\sigma}}{dt} + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma} = -ig\widehat{\sigma}\left(\widehat{b}^\dagger + \widehat{b}\right) + i\Omega_{ext}\left(2\widehat{\sigma}^\dagger\widehat{\sigma} - 1\right)\exp(-i\omega_{ext}t)/2 + \widehat{F}_\sigma(t), \tag{11.1.4}$$

$$\frac{d\widehat{b}}{dt} = (-i\omega_v - \gamma_v)\widehat{b} - ig\widehat{\sigma}^\dagger\widehat{\sigma} + \widehat{F}_b(t), \tag{11.1.5}$$

where γ_v is the damping rate of the vibrations of the molecular nuclei and $\widehat{F}_\sigma(t)$ and $\widehat{F}_b(t)$ describe the thermal noises acting on the vibrational degrees of freedom of the molecule and the dipole moment of the electronic transition from the environment, respectively (for the definition of the noise terms, see Part I, Problem 1.6, and Eq. (4.1.7), and the comments following this equation). The dissipation constant γ_σ determines the total rate of the dipole moment relaxation, which consists of the rate of radiation losses and dephasing. Keep in mind that for many molecules, the dissipation rate of the dipole moment γ_σ is mainly determined by dephasing processes [6–11]. The noises $\widehat{F}_\sigma(t)$ and $\widehat{F}_b(t)$ are associated with system losses through the fluctuation-dissipation theorem. These noises have the following correlation properties (see Problem 1.11):

$$\left\langle \widehat{F}_b(t) \right\rangle = 0, \quad \left\langle \widehat{F}_\sigma(t) \right\rangle = 0 \tag{11.1.6}$$

$$\left\langle \widehat{F}_b(t_1)\widehat{F}_b(t_2) \right\rangle = 0, \quad \left\langle \widehat{F}_\sigma(t_1)\widehat{F}_\sigma(t_2) \right\rangle = 0 \tag{11.1.7}$$

$$\left\langle \widehat{F}_b^\dagger(t_1)\widehat{F}_b^\dagger(t_2) \right\rangle = 0, \quad \left\langle \widehat{F}_\sigma^\dagger(t_1)\widehat{F}_\sigma^\dagger(t_2) \right\rangle = 0 \tag{11.1.8}$$

$$\left\langle \widehat{F}_b^\dagger(t_1)\widehat{F}_b(t_2) \right\rangle = 2\gamma_v n_v \delta(t_1 - t_2), \tag{11.1.9}$$

$$\left\langle \widehat{F}_\sigma^\dagger(t_1)\widehat{F}_\sigma(t_2) \right\rangle = \gamma_\sigma \left\langle \widehat{\sigma}^\dagger\widehat{\sigma} \right\rangle \delta(t_1 - t_2), \tag{11.1.10}$$

where $n_v = (\exp(\hbar\omega_v/T) - 1)^{-1}$ is the mean number of vibrons having the frequency ω_v in the environment of temperature T (see Eq. (11.1.27)).

The noise term $\widehat{F}_\sigma(t)$ in Eq. (11.1.4) arises from the interaction of the electronic subsystem of a molecule with the dephasing reservoir of the surrounding medium (see Remark 3.3). This interaction results in the low-frequency wing of the Mollow triplet. In the Raman experiments, this part of the spectrum is considered as immaterial nonresonant background not related to Raman scattering (see Remark 5.1). This background is usually subtracted from the spectrum to facilitate the processing of experimental data. In analytical description, such a procedure can be realized by neglecting the noise term $\widehat{F}_\sigma(t)$. Thus, system of equations (11.1.4) and (11.1.5) is simplified:

$$\frac{d\widehat{\sigma}}{dt} + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma} = -ig\widehat{\sigma}\left(\widehat{b}^\dagger + \widehat{b}\right) + i\Omega_{ext}\left(2\widehat{\sigma}^\dagger\widehat{\sigma} - \widehat{I}\right)\exp(-i\omega_{ext}t)/2 \tag{11.1.11}$$

$$\frac{d\widehat{b}}{dt} = (-i\omega_v - \gamma_v)\widehat{b} - ig\widehat{\sigma}^\dagger\widehat{\sigma} + \widehat{F}_b(t). \tag{11.1.12}$$

The system of nonlinear operator equations (11.1.11) and (11.1.12) cannot be solved analytically. However, in many practical cases, one employs the off-resonant Raman scattering when a laser with a frequency largely detuned from the electronic transition frequency of the molecule. The orders of magnitude of typical values of the relevant parameters are $\gamma_v \sim 10^{-4}$ eV, $n_v \sim 10^{-4}$, ω_σ, ω_{ext}, $\omega_\sigma - \omega_{ext}$ are optical frequencies ~1 eV (for definiteness, we assume that $\omega_\sigma > \omega_{ext}$), $\gamma_\sigma \sim 10^{-2}$ eV, $\omega_v \sim g$ lie in the IR range $\sim 10^{-3}$ eV, the Rabi frequency $\Omega_{ext} = -\mathbf{d}_{eg} \cdot \mathbf{E}_{ext}/\hbar$ is less than 10^{-3} eV at moderate values of the electric field $|\mathbf{E}(t)| < 10^6$ V/m, and a typical value of the electronic transition dipole moment is $|\mathbf{d}_{eg}| \sim 10$ D. Therefore, below, we assume that for the Rabi frequency, the following inequality is fulfilled:

$$\Omega_{ext}/\omega_\sigma \ll 1 \tag{11.1.13}$$

Let us also note that since the electron-vibron interaction should not cause electronic transitions in a TLS, we expect that $g < \omega_\sigma$. In fact, for all realistic systems, the following inequality is satisfied:

$$g/\omega_\sigma \ll 1 \tag{11.1.14}$$

Thus, our system has two small parameters:

$$\varepsilon_{\Omega_{ext}} = \Omega_{ext}/\omega_\sigma \text{ and } \varepsilon_g = g/\omega_\sigma. \tag{11.1.15}$$

The nature and origin of these parameters differ, but they have the same orders of smallness. We, therefore, can introduce a parameter $\varepsilon \sim \varepsilon_{\Omega_{ext}} \sim \varepsilon_g$, keeping in mind that ε^n corresponds to any product $\varepsilon_{\Omega_{ext}}^k \varepsilon_g^{n-k}$ with $n \geq k \geq 0$.

Developing a perturbation theory based on two small parameters can be tricky. To clarify the procedure, we introduce "dimensionless" times, $\widetilde{t}_\sigma = \omega_\sigma t$ and $\widetilde{t}_v = \omega_v t$. Using these times, we can rewrite system (11.1.11) – (11.1.12) in the form:

$$\frac{d\widehat{\sigma}}{d\widetilde{t}_\sigma} + (i + \gamma_\sigma/\omega_\sigma)\widehat{\sigma} = -i\left(\frac{g}{\omega_\sigma}\right)\widehat{\sigma}\left(\widehat{b}^\dagger + \widehat{b}\right) + i\frac{1}{2}\left(\frac{\Omega_{ext}}{\omega_\sigma}\right) \times \left(2\widehat{\sigma}^\dagger\widehat{\sigma} - \widehat{I}\right)\exp(-i\omega_{ext}t/\omega_\sigma) \tag{11.1.16}$$

$$\frac{d\widehat{b}}{d\widetilde{t}_v} = \left(-i - \frac{\gamma_v}{\omega_v}\right)\widehat{b} - i\left(\frac{g}{\omega_v}\right)\widehat{\sigma}^{\dagger}\widehat{\sigma} + \frac{1}{\omega_v}\widehat{F}_b(t). \tag{11.1.17}$$

We can see that Eq. (11.1.16) contains two small coefficients $\varepsilon_g = g/\omega_\sigma$ and $\varepsilon_\Omega = \Omega_{ext}/\omega_\sigma$ (see Eqs. (11.1.13) and (11.1.14)), while Eq. (11.1.17) does not have small parameters explicitly.

Now, we can search for unknown operators in the form of a power series:

$$\widehat{\sigma} = \widehat{\sigma}_0 + \widehat{\sigma}_1 + \ldots, \qquad \widehat{b} = \widehat{b}_0 + \widehat{b}_1 + \ldots \tag{11.1.18}$$

with $\widehat{\sigma}_n, \widehat{b}_n \sim O(\varepsilon^n)$. Here, we imply that

$$\varepsilon^n \sim \varepsilon_g^k \varepsilon_\Omega^{n-k}. \tag{11.1.19}$$

After applying expansion (11.1.18) to original system (11.1.4)–(11.1.5), we obtain a system of perturbation equations in each order in the parameter ε. In our case, the equations of the perturbation theory are reduced to the nonhomogeneous linear differential equations of the first order with respect to time. The general solution to such an equation is the sum of the general solution to the homogeneous equation and any particular solution to the nonhomogeneous equation.

In Raman scattering, we seek the molecule's oscillation spectrum when the dipole moment oscillations reach a stationary state. Since Eqs. (11.1.11) –(11.1.12) are linear, their solution is the sum of the general solution to the homogeneous equations and a partial solution to inhomogeneous equations. The general solution to the homogeneous equation is independent of the CW external field and vanishes with the rate of radiation dephasing. Further, we deal with large times, $t \gg \gamma_v^{-1}, \gamma_\sigma^{-1}$, when only driven oscillations caused by the external field survive. Therefore, the steady-state (stationary) solution reduces to the particular solution of the inhomogeneous equation; this solution becomes proportional to the external field and does not contain the information of the initial conditions. At large times, this solution is suitable for determining the spectrum. Note that vanishing in time solution generates corresponding terms in higher orders of the perturbation theory. These terms, however, also decay in time, and we neglect them in further discussion.

Now, we return to system (11.1.11)–(11.1.12). In the general case, in the n-th order, the system of perturbation equations should look as

$$\frac{d\widehat{\sigma}_n}{dt} + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_n = \widehat{I}\left(\sum\nolimits_{f=g,\Omega_{ext}} S_{f,n-1}(g,\omega_v,t) f\right)\varepsilon^{n-1} e^{-i\omega_{ext}t} \tag{11.1.20}$$

$$\frac{d\widehat{b}_n}{dt} + (i\omega_v + \gamma_v)\widehat{b}_n = \widehat{I}B_{n-1}(g,\omega_v,t) g\varepsilon^n. \tag{11.1.21}$$

In the first equation, f stands for g or Ω_{ext}. S_{n-1} and B_{n-1} are functions independent of small parameters that should be obtained while solving the equations of the $(n-1)$-th order.[2]

For times $t \gg \gamma_\sigma^{-1}, \gamma_\omega^{-1}$, for the particular solution of the nonhomogeneous equation, we obtain:

$$\widehat{\sigma}_n(t) = \left(\sum\nolimits_{f=g,\Omega_{ext}} S_{f,n}(g,\omega_v,t)\frac{f}{\omega_\sigma - \omega_{ext}}\right)\varepsilon^{n-1}e^{-i\omega_{ext}t}\widehat{I} \sim \varepsilon^n\left(\sum\nolimits_{f=g,\Omega_{ext}} S_{f,n}(g,\omega_v,t)\right)\widehat{I}.$$

$$\widehat{b}_n(t) = (g/\omega_v)\varepsilon^n B_{n-1}(g,\omega_v,t)\widehat{I} \sim \varepsilon^n B_n(g,\omega_v,t)\widehat{I}.$$

In the zeroth order of the perturbation theory, the terms proportional to Ω_{ext} and g should be omitted in Eq. (11.1.16) because they are of the first order in ε. Thus, in the zero order, there is no action of the external field, and no coupling between electronic and vibronic subsystems is taken into account, i.e., we are working with the "zeroth-order" Hamiltonian:

$$\widehat{H}_0 = \hbar\omega_0\widehat{\sigma}^\dagger\widehat{\sigma} + \hbar\omega_v\widehat{b}^+\widehat{b}.$$

Indeed, in the zeroth order on ε, Eq. (11.1.16) becomes the equation for free dipole $(\widehat{\sigma}_0)$ of the molecular electronic state:

$$\frac{d\widehat{\sigma}_0}{dt} + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_0 = 0. \tag{11.1.22}$$

At $t \gg \gamma_v^{-1}, \gamma_\sigma^{-1}$, the solution to this equation vanishes so that the stationary solution is

$$\widehat{\sigma}_0 = 0, \tag{11.1.23}$$

as expected.

For the vibron amplitude, at the zeroth order of the perturbation theory, Eq. (11.1.21) reduces to the equation:

$$\frac{d\widehat{b}_0}{dt} + (i\omega_v + \gamma_v)\widehat{b}_0 = \widehat{F}_b(t), \tag{11.1.24}$$

The solution to Eq. (11.1.24) is (see Problem 2.1)

[2] The unity operator in the right-hand side comes from the fact that the first nonzero right-hand side in the perturbation equations is proportional to $\Omega_{ext}\exp(-i\omega_{ext}t)$. The next orders can be obtained by using recursion.

$$\widehat{b}_0(t) = \widehat{b}_0(0)\exp(-(i\omega_v + \gamma_v)t) + \int_0^t \exp((-i\omega_v - \gamma_v)(t-t'))\widehat{F}_b(t')dt' \tag{11.1.25}$$

At $t \gg \gamma_\sigma^{-1}, \gamma_v^{-1}$, the stationary motion of vibrons is described by the equation:

$$\widehat{b}_0(t) = \int_0^t d\tau \exp(-(i\omega_v + \gamma_v)(t-\tau))\widehat{F}_b(\tau) \tag{11.1.26}$$

Thus, in this order, only the noise term is present on the right-hand side of Eq. (11.1.24). It means that, in the absence of an external field, the number of vibron quanta $n_v(t) \equiv \left\langle b_0^\dagger(t) b_0(t) \right\rangle$ is only determined by the coupling with the reservoir with temperature T and, therefore, should obey the Bose-Einstein statistics.

Indeed, despite the fact that $\left\langle \widehat{b}_0(t) \right\rangle = 0$, since $\left\langle \widehat{F}_b^\dagger(t_1)\widehat{F}_b(t_2) \right\rangle = 2\gamma_v n_v \delta(t_1 - t_2)$, we can find that the expectation value of $\widehat{b}_0(t)$ is equal to zero and

$$\begin{aligned}
\langle \widehat{n}_0(t) \rangle &= \left\langle \widehat{b}_0^\dagger(t)\widehat{b}_0(t) \right\rangle \\
&= \int_0^t d\tau_1 \int_0^t d\tau_2 \exp(-\gamma_v(2t - \tau_1 - \tau_2)) \exp(-i\omega_v(\tau_1 - \tau_2)) \left\langle \widehat{F}_b^\dagger(\tau_1)\widehat{F}_b(\tau_2) \right\rangle \\
&= \exp(-2\gamma_v t) \int_0^t d\tau_1 \int_0^t d\tau_2 \exp(\gamma_v(\tau_1 + \tau_2)) \exp(-i\omega_v(\tau_1 - \tau_2)) 2\gamma_v n_v \delta(\tau_1 - \tau_2) \\
&= \exp(-2\gamma_v t) 2\gamma_v n_v \int_0^t d\tau_2 \exp(2\gamma_v \tau_2) = n_v(1 - \exp(-2\gamma_v t)).
\end{aligned}$$

This equation shows that for $t \gg \gamma_v^{-1}$, the average number of vibrons is determined by the Bose-Einstein distribution:

$$\langle \widehat{n}_0(t) \rangle \simeq n_v = \frac{1}{\exp(\hbar\omega_v / kT) - 1}. \tag{11.1.27}$$

Thus, Eqs. (11.1.22) and (11.1.24) describe the situations with an unexcited TLS and incoherent vibrons generated by noises (see Eq. (11.1.25)).

Turning to the first order of the perturbation theory, in Eq. (11.1.11), we have to retain the first-order terms in ε, i.e., we take into account the TLS interactions with both the external classical field and vibrons. Since $g \sim \varepsilon$, the term having the g-prefactor may only contain additional factors $\widehat{b}_0$ and/or $\widehat{\sigma}_0$. Keeping in mind that $\widehat{\sigma}_0 = 0$, we obtain the following equations for the operators $\widehat{b}_1$ and $\widehat{\sigma}_1$:

$$\frac{d\widehat{b}_1}{dt} + (i\omega_v + \gamma_v)\widehat{b}_1 = 0. \tag{11.1.28}$$

$$\frac{d\widehat{\sigma}_1}{dt} + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_1 = -i\Omega_{ext} e^{-i\omega_{ext}t}\widehat{I}/2 \tag{11.1.29}$$

At times $t \gg \gamma_\sigma^{-1}, \gamma_v^{-1}$, the stationary solutions to Eqs. (11.1.28) and (11.1.29) are

$$\widehat{b}_1(t) = 0 \tag{11.1.30}$$

$$\widehat{\sigma}_1(t) = \widehat{I}\frac{1}{2}\frac{\Omega_{ext}}{(\omega_{ext} - \omega_\sigma)} e^{-i\omega_{ext}t} \tag{11.1.31}$$

According to Eq. (11.1.31), $\widehat{\sigma}_1(t)$ equals the identity operator multiplied by a c-number prefactor, which oscillates with the frequency of the external field. In Chap. 4, we consider such terms to be coherent. The operator $\widehat{\sigma}_1(t)$ is responsible for Rayleigh scattering.

In the second order of the perturbation theory, we restrict ourselves to considering the equation for the electronic subsystem only (see Eq. (11.1.4)). Using Eqs. (11.1.26) and (11.1.31), we obtain:

$$\begin{aligned}\frac{d\widehat{\sigma}_2}{dt} + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_2 &= -ig\widehat{\sigma}_1(t)\left(\widehat{b}_0(t) + \widehat{b}_0^\dagger(t)\right) \\ &= \frac{-ig\Omega_{ext}e^{-i\omega_{ext}t}}{2(\omega_{ext} - \omega_\sigma)} \int_0^t d\tau \left[e^{(i\omega_v - \gamma_v)(t-\tau)}\widehat{F}^\dagger{}_b(\tau) + e^{(-i\omega_v - \gamma_v)(t-\tau)}\widehat{F}_b(\tau)\right]\end{aligned} \tag{11.1.32}$$

The right-hand side of Eq. (11.1.32) contains noise terms; therefore, it is the contribution of incoherent nuclear oscillations to the response of the electronic subsystem.

The solutions to Eq. (11.1.32) and its Hermitian conjugated have the form (for details, see Problem 2.1):

$$\begin{aligned}\widehat{\sigma}_2(t) = &\frac{-ig\Omega_{ext}e^{-(i\omega_\sigma + \gamma_\sigma)t}}{2(\omega_{ext} - \omega_\sigma)} \\ &\times \int_0^t dt' \mathrm{e}^{(i\omega_\sigma + \gamma_\sigma)t'} e^{-i\omega_{ext}t'} \int_0^{t'} dt'' e^{-\gamma_v(t' - t'')}\left[e^{i\omega_v(t' - t'')}\widehat{F}_b^\dagger(t'') + e^{-i\omega_v(t' - t'')}\widehat{F}_b(t'')\right],\end{aligned} \tag{11.1.33}$$

and

$$\widehat{\sigma}_2^{\dagger}(t) = \frac{ig\Omega_{ext}e^{(i\omega_\sigma - \gamma_\sigma)t}}{2(\omega_{ext} - \omega_\sigma)} \times \int_0^t dt' \mathrm{e}^{(-i\omega_\sigma + \gamma_\sigma)t'} e^{i\omega_{ext}t'} \int_0^{t'} dt'' e^{-\gamma_v(t'-t'')} \left[e^{i\omega_v(t'-t'')}\widehat{F}_b^{\dagger}(t'') + e^{-i\omega_v(t'-t'')}\widehat{F}_b(t'') \right], \tag{11.1.34}$$

The expression $\left[e^{i\omega_v(t'-t'')}\widehat{F}_b^{\dagger}(t'') + e^{-i\omega_v(t'-t'')}\widehat{F}_b(t'') \right]$ is the sum of noise-source Fourier components with the frequencies ω_v and $(-\omega_v)$. These components are responsible for the radiation of the Stokes and anti-Stokes signals. These terms lead to the Raman effect.

Note that the coherent contribution to the oscillation of the electronic subsystem appears in the first order of the perturbation theory (see Eqs. (11.1.31) and (11.1.34)). The incoherent term for the electronic subsystem appears in the second order.

Let us find the scattering spectrum. As we discussed in Sect. 3.4.1, to calculate the spectrum, we should calculate the correlator $\left\langle \widehat{\sigma}^{\dagger}(t+\tau)\widehat{\sigma}(t) \right\rangle$.[3] Since $\widehat{\sigma}_0 = 0$, in the second order of the perturbation theory, up to the accuracy of ε^2, the approximate solution for the operator $\widehat{\sigma}$ is equal to $\widehat{\sigma}_1 + \widehat{\sigma}_2$. Therefore, we have:

$$\begin{aligned} \left\langle \widehat{\sigma}^{\dagger}(t+\tau)\widehat{\sigma}(t) \right\rangle &= \left\langle \widehat{\sigma}_1^{\dagger}(t+\tau)\widehat{\sigma}_1(t) \right\rangle + \left\langle \widehat{\sigma}_2^{\dagger}(t+\tau)\widehat{\sigma}_2(t) \right\rangle \\ &+ \left\langle \widehat{\sigma}_1^{\dagger}(t+\tau)\widehat{\sigma}_2(t) \right\rangle + \left\langle \widehat{\sigma}_2^{\dagger}(t+\tau)\widehat{\sigma}_1(t) \right\rangle \end{aligned} \tag{11.1.35}$$

From Eqs. (11.1.9), (11.1.33), and (11.1.34), we obtain:

$$\begin{aligned} \left\langle \widehat{\sigma}_1^{\dagger}(t+\tau)\widehat{\sigma}_2(t) \right\rangle &\propto \left\langle \widehat{F}_b(t) \right\rangle = 0 \\ \left\langle \widehat{\sigma}_2^{\dagger}(t+\tau)\widehat{\sigma}_1(t) \right\rangle &\propto \left\langle \widehat{F}_b^{\dagger}(t+\tau) \right\rangle = 0 \end{aligned} \tag{11.1.36}$$

Thus, the cross-terms in Eq. (11.1.35) are zero, so

$$\left\langle \widehat{\sigma}^{\dagger}(t+\tau)\widehat{\sigma}(t) \right\rangle = \left\langle \widehat{\sigma}_1^{\dagger}(t+\tau)\widehat{\sigma}_1(t) \right\rangle + \left\langle \widehat{\sigma}_2^{\dagger}(t+\tau)\widehat{\sigma}_2(t) \right\rangle \tag{11.1.37}$$

[3] To do this, we must perform two types of averaging. The first one is the averaging of the quantum mechanical operator $\widehat{\sigma}$, which we considered in Chap. 9. The second type is the averaging of the noise terms. For this purpose, we use Eq. (11.1.9) for the noise correlator, which follows from the properties of the thermal reservoir (see Chap. 9 for details). To simplify the notations, we use $\langle\rangle$ for this double averaging (i.e., averaging over the reservoir and system degrees of freedom).

Thanks to Eq. (11.1.31), we can rewrite the first term $\left\langle \widehat{\sigma}_1^{\dagger}(t+\tau)\widehat{\sigma}_1(t)\right\rangle$ in the form:

$$\left\langle \widehat{\sigma}_1^{\dagger}(t+\tau)\widehat{\sigma}_1(t)\right\rangle = \left\langle \frac{\Omega_{ext}}{2(\omega_{ext}-\omega_{\sigma})} e^{i\omega_{ext}(t+\tau)}\widehat{I}\frac{\Omega_{ext}}{2(\omega_{ext}-\omega_{\sigma})} e^{-i\omega_{ext}t}\widehat{I}\right\rangle = \frac{\Omega_{ext}^2}{4(\omega_{ext}-\omega_{\sigma})^2} e^{i\omega_{ext}\tau}. \tag{11.1.38}$$

The term $\left\langle \widehat{\sigma}_2^{\dagger}(t+\tau)\widehat{\sigma}_2(t)\right\rangle$ in Eq. (11.1.35), according to Eqs. (11.1.33) and (11.1.34), contains noise correlators. Since the noises are assumed to be Markovian, i.e., the noise at time t does not depend on the noise at previous times, the correlators have a simple form $\left\langle \widehat{F}_b^{\dagger}(t_1)\widehat{F}_b(t_2)\right\rangle = \overline{n}_v\delta(t_1-t_2)$ and $\left\langle \widehat{F}_b(t_1)\widehat{F}_b^{\dagger}(t_2)\right\rangle = (\overline{n}_v+1)\delta(t_1-t_2)$ (see Eqs. (11.1.6)–(11.1.10)). Thus, the calculation of $\left\langle \widehat{\sigma}_2^{\dagger}(t+\tau)\widehat{\sigma}_2(t)\right\rangle$ is reduced to straightforward but cumbersome mathematics. In the end (see Problem 2.2 for details of calculations), we arrive at the following result:

$$\begin{aligned}\left\langle \widehat{\sigma}^{\dagger}(t+\tau)\widehat{\sigma}(t)\right\rangle &= |S|^2\Big[\exp(i\omega_{ext}\tau) + A_{St}(1+n_v)\exp\Big(i(\omega_{ext}-\omega_v)-\frac{\gamma_v}{2}\Big)\tau \\ &\quad + A_{aSt}n_v\exp\Big(i(\omega_{ext}+\omega_v)-\frac{\gamma_v}{2}\Big)\tau\Big]\end{aligned} \tag{11.1.39}$$

where

$$S = \Omega_{ext}/2(\omega_{ext}-\omega_{\sigma}) \tag{11.1.40}$$

is the amplitude of the electric field in the Rayleigh scattering, while

$$A_{St} = g^2/\Big((\omega_{\sigma}-\omega_{ext}+\omega_v)^2+\gamma_{\sigma}^2\Big) \tag{11.1.41}$$

and

$$A_{aSt} = g^2/\Big((\omega_{\sigma}-\omega_{ext}-\omega_v)^2+\gamma_{\sigma}^2\Big) \tag{11.1.42}$$

are the intensities of the Stokes and anti-Stokes side lines normalized by the Rayleigh intensity and $n_v(t) \equiv \left\langle b_0^{\dagger}(t)b_0(t)\right\rangle$ is the number of vibron quanta determined by Eq. (11.1.27).

To obtain the scattering radiation spectrum, we should multiply the Fourier transform of the correlator defined by Eq. (11.1.39) by the factor $2(\omega_{ext}-\omega_v)^4|\mathbf{d}_{eg}|^2/3c^3$:

$$I(\omega) = \frac{2(\omega_{ext}-\omega_v)^4}{3c^3}\left|\mathbf{d}_{eg}\right|^2 \mathrm{Re}\int_0^{+\infty}\left\langle\widehat{\sigma}^{\dagger}(t+\tau)\widehat{\sigma}(t)\right\rangle e^{-i\omega\tau}d\tau$$
$$= \frac{2\omega_{ext}^4}{3c^3}\left|\mathbf{d}_{eg}\right|^2|S|^2\delta(\omega-\omega_{ext}) + \frac{2(\omega_{ext}-\omega_v)^4}{3c^3}\frac{\left|\mathbf{d}_{eg}\right|^2|S|^2A_{St}(1+n_v)\gamma_v}{(\omega_{ext}-\omega_v-\omega)^2+(\gamma_v/2)^2}$$
$$+\frac{2(\omega_{ext}+\omega_v)^4}{3c^3}\frac{\left|\mathbf{d}_{eg}\right|^2|S|^2A_{aSt}n_v\gamma_v}{(\omega_{ext}+\omega_v-\omega)^2+(\gamma_v/2)^2}. \tag{11.1.43}$$

The first term in Eq. (11.1.43) describes the Rayleigh scattering intensity, while the second and the third terms describe Stokes and anti-Stokes intensities, respectively. Unless we work in the weak coupling regime $\Omega_{ext}/\gamma_v < |\omega_{ext}-\omega_\sigma|/g$, we can neglect the Mollow triplet and obtain that the Rayleigh contribution to the spectrum has a δ-function shape. In practice, the Rayleigh contribution has a finite width determined by the linewidth of the source. The Stokes and anti-Stokes frequencies are shifted by the nuclear oscillation frequency ω_v to the low- and high-frequency regions, respectively. The Stokes and anti-Stokes contributions to the spectrum have widths determined by the damping rate of the nuclear oscillations $\gamma_v/2$ and are, therefore, incoherent contributions to the spectrum.

The ratio of the maxima of intensities of anti-Stokes and Stokes signals is determined by the number of vibrons at the reservoir temperature T:

$$\frac{A_{aSt}n_v}{A_{St}(1+n_v)} \sim \exp\left(-\frac{\hbar\omega_v}{kT}\right). \tag{11.1.44}$$

Usually, $\exp(-\hbar\omega_v/kT) \ll 1$; therefore, the Stokes signal is dominant.

To finalize, we calculate one of the important characteristics of Raman scattering, namely, the scattering cross section $\sigma_{Cross_section}$, which can be obtained by integrating the Stokes scattering radiation spectrum,

$$I_{Stokes}(\omega) = \frac{2(\omega_{ext}-\omega_v)^4}{3c^3}\frac{\left|\mathbf{d}_{eg}\right|^2|S|^2A_{St}(1+n_v)\gamma_v}{(\omega_{ext}-\omega_v-\omega)^2+(\gamma_v/2)^2}, \tag{11.1.45}$$

over the whole frequency range

$$\sigma_{Cross_section} = \frac{1}{cE^2/8\pi}\int_0^{\infty} I_{Stokes}(\omega')d\omega' \tag{11.1.46}$$

As a result, we obtain:

$$\sigma_{Cross_section}(\omega) \approx \frac{4\pi}{3} k_{St}^4 \frac{\left|\mathbf{d}_{eg}\right|^4}{\hbar^2(\omega-\omega_\sigma)^2} \frac{g^2}{(\omega_\sigma-\omega_{St})^2} \tag{11.1.47}$$

where we denote $\omega_{St} = \omega_{ext} - \omega_v$ and $k_{St} = \omega_{St}/c$.

In this chapter, we have extended the quantum theory of Rayleigh scattering developed in Sect. 6.1, to the case of Raman scattering. Within the framework of the Heisenberg picture of quantum mechanics, we could see an analogy with the behavior of the classical system and treat Raman scattering as a single process involving the forced oscillation of the molecular dipole moment by incident radiation. The intramolecular interaction between electrons and nuclei's vibrations modulates these forced oscillations, leading to Stokes and anti-Stokes lines in the emission spectrum.

To describe spontaneous Raman scattering caused by monochromatic waves, we have developed a perturbation theory that allows one to find solutions to the Heisenberg-Langevin equation. This theory uses the smallness of two coupling constants compared with the frequency ω_σ of the electronic transition of the molecule. The first small parameter $\Omega_{ext}/\omega_\sigma$ is related to the coupling constant of the external electric field with the molecular dipole moment. The second small parameter g/ω_σ is determined by the Fröhlich electron-vibron interaction constant g. In practice, both these parameters are of the same order.

The obtained operator equations of the perturbation theory are linear in each order of the small parameter, and after the transition to expectation values of operators, they can be solved analytically. Below, we use this perturbation theory to describe SERS, SRS, Raman lasing, and CARS.

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Chapter 12
Surface-Enhanced Raman Scattering (SERS)

Even though the Raman scattering cross section is extremely small [1], Raman spectroscopy has proven to be a valuable research tool. The widespread use of this method has stimulated the development of approaches to amplify the Raman signal. One of the most successful amplification methods turned out to be SERS. The essence of the method is that the Raman effect may be significantly enhanced if Raman-active molecules are adsorbed on rough metal surfaces or nanostructures. The first experiment reported on this effect [2], published in 1974, showed that the Raman signal from pyridine molecules adsorbed onto the roughened silver electrode became enhanced. The authors attributed the observed enhancement to the increased electrode surface, on which more measured molecules (analyte) were adsorbed. This qualitative explanation turns out to be incorrect. The effect was later observed not only on corrugated surfaces but on individual metallic nanoparticles and dimers [3], the surface of which was not large enough to explain the effect by increasing the number of the analyte molecules. It was shown that the effect was connected with the local enhancement of the scattered field due to the plasmonic resonance [4]. Individual metallic nanoparticles, dimers, and surface roughnesses act as local field amplifiers; in the literature, such structures are referred to as "hot points" or plasmonic nanoantennas (PNAs) (below, we use the latter term). However, the main conclusion of Ref. [2] that in order to study molecules absorbed on a metal surface by Raman spectroscopy, the surface should be rough has greatly impacted future studies.

In this chapter, we show that the magnitude of the Raman effect enhancement of a molecule placed in the vicinity of a PNA is determined by the properties of the PNA. Eventually, SERS has been associated with plasmon resonance on the substrate structure [5–9]. Below, we show that the following two types of signal enhancements turned out to be significant for SERS—the enhancement of the intensity of the incident electric field due to the plasmonic resonance and the enhancement of the radiated intensity due to the Purcell effect [10].

The Purcell effect is a change in the radiation rate of an atom placed in a resonator compared to the radiation rate of the atom in free space. This change is quantitatively

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characterized by the Purcell factor, which is defined as the ratio of relaxation rates of an atom placed in the resonator ($\gamma_{\sigma\, in\ res}$) and in vacuum ($\gamma_\sigma$):

$$F_P = \gamma_{\sigma\, in\ res}/\gamma_\sigma. \tag{12.1.1}$$

Let us recall that F_P can be expressed as the ratio of local densities of states in the resonator and vacuum. In SERS $F_P = \gamma_{\sigma\, in\ res}/\gamma_\sigma > 1$, this signifies that PNA brings in additional states, and the molecule radiates manly into the PNA states but not into free space states. The molecule plays the role of feeder for the PNA. So, the PNA emits the energy accumulated in PNA states. Thus, in SERS, it is the intensity of the PNA radiation but not the radiation of atom that is measured in experiment.

To evaluate the intensity radiated by the system consisting of the PNA and molecule, we should take into account that the radiation rate γ_S of any system is proportional to the dipole moment squared.

The size of a PNA is much larger than the size of a molecule, and the dipole moment of the PNA d_{pl} is much larger than the molecular dipole moment d_σ. Consequently, the radiation rate $\gamma_{PNA} \sim d_{pl}^2$ is much larger than that of the molecule $\gamma_\sigma \sim d_\sigma^2$, even if the molecule is placed near the PNA, $\gamma_{PNA} \gg \gamma_{\sigma\, in\ res}$. Since the PNA is fed by the radiation of the molecule, the intensity of light radiated by the PNA may be at least equal to the intensity of the molecule placed near the PNA. Due to the Purcell effect, the radiation of the PNA is F_P times larger than the intensity radiated by a single TLS [11]. This is one of the mechanisms of the SERS enhancement.

12.1 Quantum Nanoplasmonics

The term "plasmon" has appeared in plasma physics to describe longitudinal collective oscillations of electrons (Langmuir waves [12]). On average, plasma is quasineutral, i.e., the mean local charge is zero. In Ref. [12], Langmuir showed that local long-lived fluctuations with a longitudinal electric field could be excited in such a plasma. Later, such excitations came to be called "plasmons" [13]. Plasmons could arise in any medium if the value of the plasma permittivity is equal to zero. Below, to describe plasma, we employ the Drude formula for the values of plasma permittivity [14–16].

Since the electric field of a plasmon is quasistatic, we cannot quantize it using the standard scheme outlined in Sect. 2.5. To quantize the plasmon resonance, we use the following scheme. Assume that, at a certain moment of time, a spherical fluctuation in the charge distribution arises. Inside a small spherical volume, positive and negative charges move apart by a small distance dx. The new system is equivalent to two spheres of the same radius filled by positive and negative charges; the dipole moment of the system is $d = e(r_i + dx/2) - e(r_i - dx/2) = edx$. If the electron charge density is n_e, then the mean polarization of the sphere is $P = n_e d$. The field in such a sphere is equal to $-4\pi P/3$. Newton's equation of motion of an electron

$d^2x/dt^2 = eE/m_e$ may be rewritten as $ed^2x/dt^2 = e^2(-4\pi P/3)/m_e$. Then, the equation of motion for the dipole moment becomes:

$$\frac{d^2 d_{pl}}{dt^2} = \frac{4\pi e^2 n_e}{3m_e} d_{pl}. \tag{12.1.2}$$

One can see that the dipole moment performs harmonic oscillations with the frequency $\omega_{pl} = \sqrt{4\pi e^2 n_e/3m} = \omega_{pl}^0/\sqrt{3}$ [17], where ω_{pl}^0 is the plasma frequency of bulk metal. The Hamiltonian describing this system is

$$\widehat{H} = \frac{1}{2}\left(\frac{d}{dt}\widehat{d}_{pl}\right)^2 + \frac{\omega_{pl}^2 \widehat{d}_{pl}^2}{2}. \tag{12.1.3}$$

Introducing canonical (quadrature) operators

$$\widehat{q} = \widehat{d}\sqrt{\omega_{pl}/\hbar} \quad \text{and} \quad \widehat{p} = \frac{1}{\sqrt{\hbar\omega_{pl}}}\frac{d}{dt}\widehat{d}_{pl}$$

with $[\widehat{q}, \widehat{p}] = i$ permits us to determine the creation and annihilation operators:

$$\widehat{a}_{pl}^{\dagger}(t) = \frac{\widehat{q} - i\widehat{p}}{\sqrt{2}} \quad \text{and} \quad \widehat{a}_{pl}(t) = \frac{\widehat{q} + i\widehat{p}}{\sqrt{2}}, \quad \text{with} \quad \left[\widehat{a}_{pl}, \widehat{a}_{pl}^{\dagger}\right] = 1. \tag{12.1.4}$$

Using Eq. (12.1.4) we can rewrite Hamiltonian (12.1.3) in the following form:

$$\widehat{H} = \hbar\omega_{pl}\left(\widehat{a}_{pl}^{\dagger}\widehat{a}_{pl} + 1/2\right) \tag{12.1.5}$$

To finish the procedure of the plasmon quantization, we have to equate the energy of the dipole moment to the $\hbar\omega_{pl}$. To find the quantum of energy, we should calculate the energy of the polarized sphere of volume V and dipole $\mathbf{d}_{pl}$ and equate it to the energy of one quantum.

The electric field created by a sphere having the total dipole moment $\mathbf{d}$ and radius r_{sp} is

$$\mathbf{E}_d(\mathbf{r}) = \begin{cases} -\mathbf{d}_{pl}/a^3, & r < r_{sp}, \\ \left(3\left(\mathbf{n}\cdot\mathbf{d}_{pl}\right)\mathbf{n} - \mathbf{d}_{pl}\right)/r^3, & r > r_{sp} \end{cases}. \tag{12.1.6}$$

We have assumed that inside, the sphere is uniformly polarized with the polarization $P = d_{pl}/(4\pi a^3/3)$. The energy of this electric field should be equal to the energy of one quantum:

$$\hbar\omega_{pl} = \frac{1}{8\pi}\int\limits_V d^3\mathbf{r}\frac{\partial(\omega\varepsilon(\omega))}{\partial\omega}|\mathbf{E}_d(\mathbf{r})|^2. \tag{12.1.7}$$

Here and below in this section, we suppose that the permittivity inside the metal nanoparticle ε_{in} can be described by the Drude formula:

$$\varepsilon_{in}(\omega) = 1 - \frac{\left(\omega_{pl}^0\right)^2}{\omega^2}, \tag{12.1.8}$$

while the medium outside of the nanoparticle is vacuum, i.e., $\varepsilon_{out} = 1$.

Using $\partial\varepsilon_{out}/\partial\omega = 0$, we can write:

$$\begin{aligned}\frac{1}{8\pi}\int\limits_V d^3\mathbf{r}\frac{\partial(\omega\varepsilon(\omega))}{\partial\omega}|\mathbf{E}_d(\mathbf{r})|^2 &= \frac{1}{8\pi}\frac{\partial(\varepsilon_{in}(\omega))}{\partial\omega}\int\limits_{V_{in}} d^3\mathbf{r}|\mathbf{E}_d(\mathbf{r})|^2 \\ &+\frac{1}{8\pi}\int\limits_{V_{in}} d^3\mathbf{r}\varepsilon_{in}(\omega)|\mathbf{E}_d(\mathbf{r})|^2 + \frac{1}{8\pi}\int\limits_{V_{out}} d^3\mathbf{r}\varepsilon_{out}(\omega)|\mathbf{E}_d(\mathbf{r})|^2\end{aligned} \tag{12.1.9}$$

By virtue of Maxwell's equation, $\nabla\cdot(\varepsilon\mathbf{E}) = 0$, and the boundary condition $\mathbf{n}\cdot\mathbf{E}_{d,\ in}(\mathbf{r})\varepsilon_{in}(\omega) = \mathbf{n}\cdot\mathbf{E}_{d,\ out}(\mathbf{r})\varepsilon_{out}(\omega)$, the sum of the last two terms on the right-hand side of Eq. (12.1.9) is zero. Indeed,

$$\begin{aligned}\int_\Omega \varepsilon\mathbf{E}\cdot\mathbf{E}\,dV &= -\int_\Omega \varepsilon\mathbf{E}\cdot\nabla\varphi\,dV \\ &= -\int_\Omega[\nabla\cdot(\varphi\varepsilon\mathbf{E}) - \varphi\nabla\cdot(\varepsilon\mathbf{E})]\,dV = \oint_{A_\Omega}\varphi(\varepsilon\mathbf{E}\cdot\mathbf{n})\,dA = 0.\end{aligned}$$

Integrating over the internal volume of the sphere, we obtain:

$$\begin{aligned}\hbar\omega_{pl} &= \frac{1}{8\pi}\int\limits_V d^3\mathbf{r}\frac{\partial(\omega\varepsilon(\omega))}{\partial\omega}|\mathbf{E}_d(\mathbf{r})|^2 \\ &= \frac{1}{8\pi}\frac{\partial(\varepsilon_{in}(\omega))}{\partial\omega}\int\limits_{V_{in}} d^3\mathbf{r}|\mathbf{E}_d(\mathbf{r})|^2 = \frac{1}{8\pi}\frac{\partial(\varepsilon_{in}(\omega))}{\partial\omega}\left|\frac{\mathbf{d}_{pl}}{a^3}\right|^2 V_{\text{int}} \\ &= \frac{1}{8\pi}\frac{2\left(\omega_{pl}^0\right)^2}{\omega_{pl}^2}\frac{|\mathbf{d}_{pl}|^2}{a^6}\frac{4\pi a^3}{3} = \frac{d_{pl}^2}{a^3}.\end{aligned} \tag{12.1.10}$$

Thus,

$$d_{pl} = \sqrt{\hbar\omega_{pl}a^3} = \sqrt{3\hbar\omega_{pl}V/4\pi} \tag{12.1.11}$$

Finally, we obtain the operator of the dipole moment in terms of the creation and annihilation operators (Eq. (12.1.4)):

$$\widehat{d}_{pl} = \sqrt{3\hbar\omega_{pl}V/4\pi}\left(\widehat{a}^{\dagger}_{pl} + \widehat{a}_{pl}\right). \tag{12.1.12}$$

Thanks to Eq. (12.1.6), the latter definition of the quantum of the dipole moment determines the quantum of plasmon (the field of the PNA).

12.2 Enhancement of the Radiated Field Intensity Due to the Purcell Effect

At the end of the nineteenth century, Hertz experimentally discovered an increase in the intensity radiating by an emitter placed near a resonant antenna. The emitter plays the role of the feeder, while the antenna acts as a mediator that improves the impedance between the emitter and free space while the total energy is conserved.

In a quantum system, thanks to the Purcell effect, the radiation rate of an atom placed in a resonator can be enhanced by the factor F_P (see Eq. (12.1.1)). Thus, one can control the EM radiation rate of a molecule by changing the environment (see Fig. 12.1). In the simplest case of a system consisting of a quantum emitter and a plasmonic resonator, this effect is manifested as a change in the emission rate [18–23].

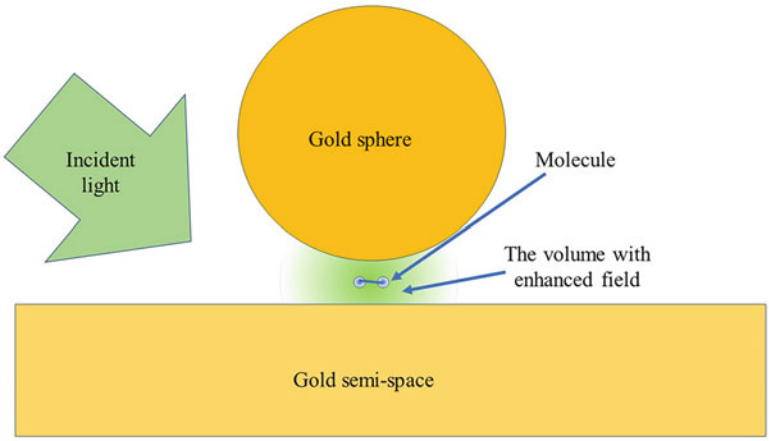

Fig. 12.1 The schematics for the PNA consisting of a gold sphere and a gold substrate. Even though, in the text, we model PNA by a sphere, in practice, more realistic shapes of PNAs are used

Below, we are interested in the radiation of a molecule placed near a PNA. The molecule (quantum emitter) is modeled as an effective TLS, and the PNA is considered as a resonator, in which the EM field is described as a harmonic oscillator. We assume that we deal with a resonant case in which the TLS transition frequency and the PNA eigenfrequency are the same, and the excitation of the TLS causes the excitation of a plasmon by the nonradiative Förster mechanism, which assumes that the TLS-PNA interaction is of the dipole-dipole nature [24, 25] and the electric field of the TLS excites the plasmon. Consequently, the TLS excitation relaxes. The Hamiltonian that describes this process can be written analogously to that of the excitation of the EM mode in the Rabi oscillations:

$$\widehat{H} = \hbar\omega_\sigma \widehat{\sigma}^\dagger \widehat{\sigma} + \hbar\omega_{pl} \widehat{a}_{pl}^\dagger \widehat{a}_{pl} + \hbar\Omega_{R\,pl}\left(\widehat{a}_{pl}\widehat{\sigma}^\dagger + \widehat{a}_{pl}^\dagger \widehat{\sigma}\right) \tag{12.1.13}$$

Consequently, the coupling constant between the TLS and the PNA mode (the Rabi frequency) takes the form:

$$\Omega_{R\,pl} \sim \mathbf{d}_{eg} \cdot \mathbf{d}_{pl} / \left(\hbar a^3\right) = \sqrt{4\pi\omega_{pl}/(3\hbar V_{PNA})}\left|\mathbf{d}_{eg}\right| / (\hbar 3V 4\pi). \tag{12.1.14}$$

Below, we suppose that the size of the PNA is so large (≥50nm) that radiation losses are much larger than the ohmic losses. In such a case, the relaxation rate γ_σ of the dipole moment of the TLS placed in vacuum is proportional to d_{eg}^2 (see Eq. (3.1.20)), while the relaxation rate of the plasmon γ_{pl}, responsible for radiation losses of the PNA, is proportional to the square of the dipole moment of the localized plasmon d_{pl}. Since the size of the PNA is much larger than that of the TLS, it is assumed that $d_{pl}/d_{eg} \gg 1$. Therefore, we can write the following inequality [26, 27]:

$$\gamma_{pl}/\gamma_\sigma \approx \left(d_{pl}/d_{eg}\right)^2 = \alpha^2 \gg 1 \tag{12.1.15}$$

Hamiltonian (12.1.13) allows us to write the Heisenberg-Langevin equations for the involved operators. For estimations, it is convenient to transition to observables of the operators $a_{pl} = \langle \widehat{a}_{pl} \rangle$, $\sigma = \langle \widehat{\sigma} \rangle$, and $D = \left\langle 2\widehat{\sigma}^\dagger \widehat{\sigma} - 1 \right\rangle$ and make the commonly used approximation $\left\langle \widehat{D}\widehat{a}_{pl} \right\rangle = \left\langle \widehat{D} \right\rangle \langle \widehat{a}_{pl} \rangle$ [24, 26]. As a result, we arrive at the Maxwell-Bloch equations for c-numbers:

$$\frac{d}{dt} a_{pl} = \left(-i\omega_\sigma - \gamma_{pl}\right) a - i\Omega_{R\,pl}\sigma \tag{12.1.16}$$

$$\frac{d}{dt}\sigma = -i\omega_\sigma \sigma - \gamma_\sigma \sigma + i\Omega_{R\,pl} D a_{pl} \tag{12.1.17}$$

$$\frac{d}{dt}D = 2i\Omega_{R\,pl}\left(a_{pl}^{*}\sigma - a_{pl}\sigma^{*}\right) - \gamma_D(D+1) \tag{12.1.18}$$

where γ_D is the relaxation rate of the inverse population of the TLS. Assuming that the effect is resonant, we put $\omega_\sigma = \omega_{pl}$.

In the *strong coupling regime*, $\Omega_{R\,pl}^2 \gg \left(\gamma_\sigma - \gamma_{pl}\right)^2/4$, the power transferred from the TLS to the PNA is so large that the energy is transferred from the quantum emitter to the PNA and back with the Rabi frequency. Thus, the effect of the Rabi oscillations (the Raby splitting) prevails over the process of radiation (see Sects. 2.1 and 2.2 and Refs. [28, 29]).

The physics of the *weak coupling regime*, in which

$$\Omega_{R\,pl}^2 \ll \left(\gamma_{pl} - \gamma_\sigma\right)^2/4, \tag{12.1.19}$$

is more interesting. Since $\gamma_\sigma \ll \gamma_{pl}$, the inequality (12.1.19) reduces to $\Omega_{R\,pl}^2 \ll \gamma_{pl}^2/4$.

We are interested in the process of relaxation of the excited atom into PNA during the time $t \sim 1/\gamma_{pl}$. Consequently, the inverse population D changes insignificantly; therefore, we can put $D = D_0 = -1$. Then, from Eqs. (12.1.16) and (12.1.17), we obtain:

$$\frac{d}{dt}a_{pl} = -i\omega_\sigma a_{pl} - \gamma_{pl}a_{pl} - i\Omega_{R\,pl}\sigma \tag{12.1.20}$$

$$\frac{d}{dt}\sigma = -i\omega_\sigma\sigma - \gamma_\sigma\sigma - i\Omega_{R\,pl}a_{pl} \tag{12.1.21}$$

The eigenfrequencies ω of system (12.1.20) and (12.1.21) are determined by the equation:

$$\left(i\omega - i\omega_{pl} - \gamma_{pl}\right)\left(i\omega - i\omega_\sigma - \gamma_\sigma\right) + \Omega_{R\,pl}^2 = 0. \tag{12.1.22}$$

In what follows, we focus on the imaginary parts $\gamma_{\sigma\pm}$ of $\omega_\pm$. The expression for eigenfrequencies (12.1.24) defines several regimes of system operations depending on the relationship between the Rabi frequency $\Omega_{R\,pl}$ and the loss rates γ_σ and γ_{pl}. Since the size and the dipole moment of the PNA are much greater than those of the TLS, the PNA should radiate better than the TLS. Consequently, we assume that $\gamma_{pl} \gg \gamma_\sigma$. Thus, we may neglect small terms proportional to $(\Omega_{R\,pl}/\gamma_{pl})^2$ in Eq. (12.1.24). However, since we expect the PNA to radiate better than the TLS, we assume that $\gamma_{pl} \gg \gamma_\sigma$ and that $\Omega^2/\gamma_{pl}\gamma_\sigma \gg 1$ even though $(\Omega_{R\,pl}/\gamma_{pl})^2 \ll 1$. Therefore, we retain the terms containing the product $(\gamma_{pl}/\gamma_\sigma)(\Omega_{R\,pl}/\gamma_{pl})^2 = (\Omega_{R\,pl}/\gamma_\sigma)(\Omega_{R\,pl}/\gamma_{pl})$.

There are two solutions to Eq. (12.1.22):

$$\omega = \omega_\sigma - i\frac{\gamma_{pl}+\gamma_\sigma}{2} \pm \sqrt{\Omega^2 - \left(\gamma_{pl}-\gamma_\sigma\right)^2/4} \tag{12.1.23}$$

Since we consider the weak coupling limit, $\Omega^2 \ll (\gamma_{pl} - \gamma_\sigma)^2/4$, we can expand the square root in Eq. (12.1.23). The root with the "plus" sign has the form:

$$\omega_+ = \omega_\sigma - i\gamma_\sigma\left(1 + \left(\gamma_{pl}/\gamma_\sigma\right)\Omega^2_{R\,pl}/\left(\gamma_{pl}\right)^2\right) \tag{12.1.24}$$

The corresponding eigenvector is

$$a_+ \approx -i\frac{\Omega^2_{R\,pl}}{\gamma_{pl}} \ll 1, \sigma_+ \approx 1. \tag{12.1.25}$$

The "minus" root has the form:

$$\omega_- = \omega_\sigma - i\gamma_{pl}, \tag{12.1.26}$$

while the corresponding eigenvector is

$$a_- \approx 1, \sigma_- \approx i\frac{\Omega_{R\,pl}}{\gamma_{pl}} \ll 1 \tag{12.1.27}$$

When initially the TLS is not excited, but the PNA is excited ($a(0) \approx 1$, $\sigma(0) \approx 0$), in the expansion of the initial conditions into eigenstates of Eqs. (12.1.20) and (12.1.21), the main contribution is produced by eigenvector (12.1.27) with the eigenfrequency ω_-. Unsurprisingly, the system relaxed with the rate $\mathrm{Im}\omega_- = \gamma_{pl}$ radiating into free space.

If, initially, the TLS is excited ($\sigma(0) = \sigma_0 \neq 0$) and the PNA is not ($a(0) = 0$), the solution to Eqs. (12.1.20) and (12.1.21) is a linear combination of eigenvectors (12.1.25), and the main contribution is produced by eigenvector (12.1.27) with the eigenfrequency ω_-. Thus, the solutions for the PNA interacting with the TLS are

$$\sigma(t) = \sigma_0 \exp\left[-i\omega_\sigma t - \gamma_\sigma\left(1 + \Omega^2_{R\,pl}/\gamma_\sigma\gamma_{pl}\right)t\right] \tag{12.1.28}$$

$$a_{pl}(t) = \sigma_0\frac{\Omega_{R\,pl}}{\gamma_{pl}}\left(\exp\left[\left(-i\omega_\sigma - \gamma_{pl}\right)t\right] - 1\right) \tag{12.1.29}$$

From Eq. (12.1.28) we can see that the modified relaxation rate of a TLS dipole is equal to

$$\gamma_{\sigma\, in\ res} = \gamma_\sigma \left[1 + \frac{\gamma_{pl}}{\gamma_\sigma} \left(\frac{\Omega_{R\, pl}}{\gamma_{pl}} \right)^2 \right]$$

and it can be expressed via the Purcell factor:

$$F_P = \frac{\gamma_{\sigma\, in\ res}}{\gamma_\sigma} = 1 + \frac{\Omega_{R\, pl}^2}{\gamma_{pl}\gamma_\sigma} = 1 + \frac{\Omega_{R\, pl}^2 \alpha^2}{\gamma_{pl}^2} \gg 1 \tag{12.1.30}$$

where $\alpha = d_{pl}/d_{eg} = \sqrt{\gamma_{pl}/\gamma_\sigma}$.

In Ref. [30], Purcell stated (but not derived) that F_P is proportional to the density of modes in the surrounding medium or to the Q-factor:

$$F_P = \frac{\gamma_{Fp}}{\gamma_\sigma} = \frac{\lambda^3}{4\pi^2} \frac{Q_{pl}}{V}.$$

For a plasmonic system, Eq. (3.1.23) gives the following expression for the rate of spontaneous radiation by a dipole into the free space modes:

$$\gamma_D = \pi \Omega^2(\omega_\sigma) \Pi_0(\omega_\sigma) = \frac{4 d_{eg}^2 \omega_\sigma^3}{3c^3 \hbar}, \tag{12.1.31}$$

where $\Pi_0 = V\omega^2/3\pi^2 c^3$ is the density of states in free space. Following Purcell, we use the density of states of the PNA modes instead of Π_0. This density of states can be found if we consider the PNA as a resonator into which the TLS relaxes. This is a separate problem that is outside the scope of this book. Here, we only give an estimate for the PNA density of states $\Pi_{PNA}(\omega)$. Considering the PNA as a resonant dipole antenna, we approximate the density of states with the Lorentz formula [31]:

$$\Pi_{PNA}(\omega) = \frac{1}{\pi\gamma_{pl}} \frac{\left(\gamma_{pl}\right)^2}{\left(\left(\omega - \omega_{pl}\right)^2 + \left(\gamma_{pl}\right)^2\right)} = \frac{2}{\pi\gamma_{pl}^{(rad)}} \frac{\left(\gamma_{pl}^{(rad)}/2\right)^2}{\left(4\left(\omega - \omega_{pl}\right)^2 + \left(\gamma_{pl}^{(rad)}/2\right)^2\right)}, \tag{12.1.32}$$

where V is the volume of the mode and $\gamma_{pl} = \gamma_{pl}^{(rad)}/2$. Taking into account that the quality factor $Q_{PNA} = \omega_{pl}/(2\gamma_{pl})$ or

$$2\gamma_{pl} = \omega_{pl}/Q_{cav}, \tag{12.1.33}$$

at the resonant frequency, $\omega = \omega_{pl}$, we obtain (see Eq. (12.1.32) and Refs. [32, 33]):

$$\Pi_{PNA}(\omega_{pl}) = \frac{2}{\pi\gamma_{pl}}. \tag{12.1.34}$$

Then, using Eq. (12.1.33), we have $\frac{2}{\pi\gamma_{pl}} = \frac{2Q_{PNA}}{\pi\omega_{pl}}$.

For a TLS radiating in vacuum ($\Omega_R = E_0 d_{eg} = \sqrt{2\pi\omega_{pl}/V\hbar}$ and $\Pi_0 = V\omega^2/3\pi^2c^3$), we obtain (see Eq. (3.1.21)):

$$\gamma_D^{(vac)} = 2\gamma_\sigma^{(vac)} = 2\pi\Omega_R^2(\omega_\sigma)\Pi_0(\omega_\sigma) = 2\frac{2\pi^2\omega_\sigma d_{eg}^2}{V\hbar}V\frac{\omega_\sigma^2}{3\pi^2c^3} = \frac{4d_{eg}^2\omega_\sigma^3}{3c^3\hbar}. \tag{12.1.35}$$

For a TLS radiating in a PNA, which localizes the plasmon, we have (Eq. (12.1.14)):

$$\Omega_{R\,pl} = d_{pl}d_{eg}/(\hbar a)^3 = d_{eg}\sqrt{(4\pi/3V)\omega_{pl}/\hbar} \quad \text{and} \quad \Pi_{pl}(\omega_0) = 2Q/(\pi\omega_0).$$

Using Eq. (12.1.34) we obtain:

$$\gamma_D^{(cav)} = 2\gamma_\sigma^{(vac)} = 2\pi\Omega_R^2(\omega_\sigma)\Pi_{pl}(\omega_\sigma) = \frac{4\pi\omega_\sigma d_{eg}^2}{3\hbar V}\frac{2Q_{cav}}{\pi\omega_{pl}} = \frac{8\pi d_{eg}^2 Q_{cav}}{3V\hbar}. \tag{12.1.36}$$

Finally, we can see that the Purcell factor is proportional to the ratio of the density of states in a plasmonic resonator to that in vacuum: $F_P = \gamma_{\sigma\,in\ res}/\gamma_\sigma$

$$F_P = \frac{\gamma_{Fp}}{\gamma_\sigma} = \frac{8\pi d_{eg}^2 Q_{cav}}{3V\hbar}\Big/\frac{4d_{eg}^2\omega_\sigma^3}{3c^3\hbar} = \frac{8\pi d_{eg}^2 Q_{cav}}{3V\hbar}\frac{3\hbar}{4d_{eg}^2(\omega_\sigma/c)^3} = \frac{\lambda^3}{4\pi^2}\frac{Q_{cav}}{V}. \tag{12.1.37}$$

As was shown above, the essence of the Purcell effect is that the energy from a TLS is not emitted into free space but is transferred to plasmon oscillations. It is the radiation emitted by these plasmons that is observed in the experiment.

Note that increasing the Purcell factor does not enhance the Raman signals. It only causes an increase in the energy reserve in the plasmonic resonator. To achieve signal enhancement, it is necessary to increase the radiation intensity of the resonator (in our case, the PNA). We also need to use an optimal value of the quality factor [34]. The existence of such a value follows from the following arguments. On the one hand, an increase in the Purcell factor indicates an increase in the power feeding the PNA. This increase is proportional to the quality factor of the PNA (Eq. (12.1.37)). On the other hand, the radiation rate of the PNA is inversely proportional to its quality factor (see Eq. (12.1.33)). This optimum value is achieved when $\gamma_{Fp} = F_p\gamma_\sigma$ and $\gamma_{cav}^{(rad)} = \omega_{pl}/Q_{cav}$. When this condition is met, each photon transmitted to the PNA is emitted. There is no useless accumulation of energy in plasma oscillations. Thus, the optimal value of the quality factor is determined by the equality $(\lambda^3/4\pi^2)(Q_{cav}^{opt}/V)\gamma_\sigma = \omega_{pl}/Q_{cav}^{opt}$ so that

$$Q_{cav} = 2\pi\sqrt{\left(\omega_{pl}/\gamma_{\sigma}\right)\left(V/\lambda^3\right)} \tag{12.1.38}$$

The smaller the volume of the PNA mode, the smaller is the required optimal quality factor. This explains why using low-Q subwavelength plasmonic resonators is more efficient than high-Q dielectric resonators with a size larger than the wavelength. Indeed, we can achieve high Q for the dielectric resonator, but to achieve at optimal regime, a large volume is needed $\gamma_{Fp} = F_p\gamma_{\sigma} \sim \left(Q_{cav}^{opt}/V\right)$. Thus, using the dielectric resonator does not lead to an increase in the radiation intensity.

Let us give estimates for the Purcell factor in some cases. In the microwave range, in which the resonator size may be as large as $V \sim (100\lambda)^3$ and $Q \approx 10^4$, the optimal Purcell factor is small enough, $F_P \approx 4 \times 10^{-3}$. In optics, high-$Q$ resonators are fabricated using the whispering gallery modes. Unfortunately, decreasing the size of the resonator leads to a sharp decrease in the quality factor [35]. Hence, in optics, the resonators made of dielectrics cannot provide large Purcell factors. In plasmonics, despite the low Q-factor ($Q \sim 10$), the Purcell factor can have high values $F_P \approx 4 \times 10^2$ due to the small plasmonic mode volume, $V \sim (\lambda/10)^3$.

If the dipole moment of a localized plasmon d_p is much larger than the molecular dipole moment d_{eg}, then the radiation intensity of the PNA exceeds the radiation losses of the molecule by F_P and prevails in radiation of the elementary SERS system—plasmon-molecule.

In the next section, we show that the Purcell effect can significantly increase the intensity of spontaneous Raman scattering for a molecule placed near a PNA.

12.3 Description of SERS by Heisenberg-Langevin Equations

To describe the SERS effect, we have to take into account both the excitation of plasmons and their interaction with the molecule. For this, we have to modify Hamiltonian (10.1.23) by adding plasmon-related terms:

$$\begin{aligned}\widehat{H}_S = {} & \hbar\omega_{\sigma}\widehat{\sigma}^{\dagger}\widehat{\sigma} + \hbar\omega_{v}\widehat{b}^{\dagger}\widehat{b} + \hbar g\widehat{\sigma}^{\dagger}\widehat{\sigma}\left(\widehat{b}^{\dagger} + \widehat{b}\right) + \frac{\hbar\Omega_{ext}}{2}\left(\widehat{\sigma}^{\dagger}e^{-i\omega_{ext}t} + \widehat{\sigma}e^{i\omega_{ext}t}\right) \\ & + \hbar\omega_{pl}\widehat{a}_{pl}^{\dagger}\widehat{a}_{pl} + \alpha\frac{\hbar\Omega_{ext}}{2}\left(\widehat{a}_{pl}^{\dagger}e^{-i\omega_{ext}t} + \widehat{a}_{pl}e^{i\omega_{ext}t}\right) + \hbar\Omega_{R\,pl}\left(\widehat{\sigma}^{\dagger}\widehat{a}_{pl} + \widehat{\sigma}\widehat{a}_{pl}^{\dagger}\right),\end{aligned} \tag{12.2.1}$$

The last two terms in this Hamiltonian describe the plasmon interaction with the external field and the TLS-plasmon coupling, respectively. The relationship between corresponding coupling constants is [36]

$$\Omega_{R\,pl} = \sqrt{\left(4\pi\hbar\omega_{pl}\right)/3V_{PNA}}\left|\mathbf{d}_{pl}\right| = -\mathbf{d}_{pl}\cdot\mathbf{E}_{ext}/\hbar = \alpha\Omega_{ext}$$

where $\alpha^2 = \gamma_{pl}/\gamma_\sigma \approx (d_{pl}/d_{eg})^2 \gg 1$.

In the same way, as we considered spontaneous Raman scattering, we obtain the Langevin-Heisenberg operator equations with noises for the nuclear vibration operator $\widehat{b}$, the TLS operator $\widehat{\sigma}$, and the localized plasmon operator $\widehat{a}_{pl}$:

$$d\widehat{b}/dt = (-i\omega_v - \gamma_v)\widehat{b} - ig\widehat{\sigma}^\dagger\widehat{\sigma} + \widehat{F}_b(t), \tag{12.2.2}$$

$$d\widehat{\sigma}/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma} = \left(i\frac{\Omega_{ext}}{2}e^{-i\omega_{ext}t} + i\Omega_{R\,pl}a_{pl}\right)\left(2\widehat{\sigma}^\dagger\widehat{\sigma} - 1\right) - ig\widehat{\sigma}\left(\widehat{b}^\dagger + \widehat{b}\right) + \widehat{F}_\sigma(t), \tag{12.2.3}$$

$$d\widehat{a}_{pl}/dt = \left(-i\omega_{pl} - \gamma_{pl}\right)\widehat{a}_{pl} - i\Omega_{R\,pl}\widehat{\sigma} - i\alpha\frac{\Omega_{ext}}{2}e^{-i\omega_{ext}t} + \widehat{F}_a(t). \tag{12.2.4}$$

To see the relationship between nanoparticle parameters, let us consider a silver nanoparticle where the Joule losses are minimal in the visible frequency range. There is the hope of finding more suitable materials [33].

If the size of a silver nanoparticle is greater than 50 nm, then the radiation losses are greater than the Joule losses, and radiative damping is the main channel for the relaxation of plasmons in the metal nanoparticles [37]. Consequently, $\gamma_\sigma \simeq \gamma_D^{free}/2$ (where $\gamma_D^{free} = 4\omega_\sigma^3\left|\mathbf{d}_{eg}\right|^2/3\hbar c^3$) and $\gamma_{pl} = \gamma_{D\,pl}^{free}/2$ (where $\gamma_{D\,pl}^{free} = 4\gamma\omega_{pl}^3\left|\mathbf{d}_{pl}\right|^2/3\hbar c^3$) are the rates of radiation losses in the free molecule and the plasmonic nanoparticle, respectively.

Further, we assume that the transition energy of a TLS and the plasmon excitation energy are much greater than the system temperature, $\hbar\omega_\sigma$, $\hbar\omega_{pl} \gg kT$, as is usually the case in quantum optics. We have seen in Chap. 11 that the strength of the noise is proportional to the mean value of the number of quanta $\overline{n}(\omega_v) = \left(\exp(\hbar\omega_v/kT) - 1\right)^{-1}$ in the reservoir. Since ω_{ext}, $\omega_{pl} \gg \omega_v$, we can neglect the noises in the TLS and PNA, which are proportional to $\overline{n}(\omega_a) = \left(\exp(\hbar\omega_a/kT) - 1\right)^{-1}$) compared to the noise of the nuclear vibrations, and put $\widehat{F}_\sigma(t) = 0$ and $\widehat{F}_a(t) = 0$. Then, Heisenberg-Langevin equations (12.2.2)–(12.2.4) take the form:

$$d\widehat{b}/dt + (i\omega_v + \gamma_v)\widehat{b} = -ig\widehat{\sigma}^\dagger\widehat{\sigma} + \widehat{F}_b(t), \tag{12.2.5}$$

$$d\widehat{\sigma}/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma} = -ig\widehat{\sigma}\left(\widehat{b}^\dagger + \widehat{b}\right) + \left(i\frac{\Omega_{ext}}{2}e^{-i\omega_{ext}t} + i\Omega_{R\,pl}a\right)\left(2\widehat{\sigma}^\dagger\widehat{\sigma} - 1\right), \tag{12.2.6}$$

$$d\widehat{a}_{pl}/dt + \left(i\omega_{pl} + \gamma_{pl}\right)\widehat{a}_{pl} = -i\Omega_{R\,pl}\widehat{\sigma} - i\alpha\Omega_{ext}e^{-i\omega_{ext}t}/2, \tag{12.2.7}$$

We assume that the external field is not too high, and despite that $\Omega_{R\,pl} \sim \alpha\Omega_{ext} \gg \Omega_{ext}$, the following inequalities are satisfied:

$$\Omega_{ext}/\omega_\sigma \ll 1, \quad \Omega_{R\,pl}/\omega_\sigma \ll 1, \quad g/\omega_\sigma \ll 1 \tag{12.2.8}$$

Following the procedure developed in Chap. 3, we use a small parameter $\varepsilon \sim \Omega/\omega_\sigma \sim g/\omega_\sigma$ to search for a solution to Eqs. (12.2.5)–(12.2.7) in the form of a series of the perturbation theory:

$$\widehat{\sigma} = \widehat{\sigma}_0 + \widehat{\sigma}_1 + \widehat{\sigma}_2 \ldots, \qquad \widehat{a} = \widehat{a}_0 + \widehat{a}_1 + \widehat{a}_2 \ldots, \qquad \widehat{b} = \widehat{b}_0 + \widehat{b}_1 + \widehat{b}_2 \ldots \tag{12.2.9}$$

where $\widehat{\sigma}_n, \widehat{a}_n, \widehat{b}_n \sim O(\varepsilon^n)$. Substituting this series into Eqs. (12.2.5)–(12.2.7), we obtain the equations that govern the quantities of the same orders of the perturbation theory.

In the zeroth order, there are no plasmons, no action of an external field, and *no coupling between electronic and vibronic subsystems* ($\widehat{a}_0 = 0$); Eqs. (12.2.5)–(12.2.7) are simplified:

$$d\widehat{b}_0/dt + (i\omega_v + \gamma_v)\widehat{b}_0 = \widehat{F}_b(t), \tag{12.2.10}$$

$$d\widehat{\sigma}_0/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_0 = 0 \tag{12.2.11}$$

$$d\widehat{a}_{0pl}/dt + (i\omega_a + \gamma_a)\widehat{a}_{0pl} = 0. \tag{12.2.12}$$

The solution to Eq. (12.2.10) is

$$\widehat{b}_0(t) = \int_0^t d\tau \exp(-(i\omega_v + \gamma_v)(t-\tau))\widehat{F}_b(\tau) \tag{12.2.13}$$

The stationary solutions to Eqs. (12.2.11) and (12.2.12) are

$$\widehat{\sigma}_0 = 0 \tag{12.2.14}$$

$$\widehat{a}_0 = 0 \tag{12.2.15}$$

The number of incoherent nuclear vibrations depends on the ambient temperature T only, and it is determined by (11.1.27).

In the first order of the perturbation theory, equations of motion (12.2.5)–(12.2.7) are

$$d\widehat{b}_1/dt + (i\omega_v + \gamma_v)\widehat{b}_1 = 0, \tag{12.2.16}$$

$$d\widehat{\sigma}_1/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_1 = -i\Omega_{R\,pl}\widehat{a}_1 - \frac{i}{2}\Omega_{ext}e^{-i\omega_{ext}t}, \tag{12.2.17}$$

$$d\widehat{a}_{pl\,1}/dt + (i\omega_{pl} + \gamma_{pl})\widehat{a}_{pl\,1} = -i\Omega_{R\,pl}\widehat{\sigma}_1 - i\frac{\alpha}{2}\Omega_{ext}e^{-i\omega_{ext}t}. \tag{12.2.18}$$

The particular solutions to Eqs. (12.2.17) and (12.2.18) are

$$\widehat{\sigma}_1 = \widehat{I}\frac{1}{2}\frac{-\alpha\Omega_{R\,pl} - \left(i\left(\omega_{ext} - \omega_{pl}\right) + \gamma_{pl}\right)}{\left(-i(\omega_{ext} - \omega_\sigma) + \gamma_\sigma\right)\left(-i\left(\omega_{ext} - \omega_{pl}\right) + \gamma_{pl}\right) + \Omega_{R\,pl}^2}\Omega_{ext}\exp(-i\omega_{ext}t), \tag{12.2.19}$$

$$\widehat{a}_{pl\,1} = \widehat{I}\frac{1}{2}\frac{-\Omega_{R\,pl} - \alpha\left(i\left(\omega_{ext} - \omega_{pl}\right) + \gamma_{pl}\right)}{\left(-i(\omega_{ext} - \omega_\sigma) + \gamma_\sigma\right)\left(-i\left(\omega_{ext} - \omega_{pl}\right) + \gamma_{pl}\right) + \Omega_{R\,pl}^2}\Omega_{ext}\exp(-i\omega_{ext}t). \tag{12.2.20}$$

They describe the Rayleigh scattering.

The stationary solution to Eq. (12.2.16) is

$$b_1 = 0 \tag{12.2.21}$$

Below, we express the enhanced amplitudes of $\widehat{\sigma}_1$ and $\widehat{a}_{pl1}$ through the Purcell factor. For this purpose, we have to take into account that usually, in SERS experiments, the frequency of the external field is inside the plasmonic resonance line, $|\omega_{ext} - \omega_{pl}| \le \gamma_{pl}$, and in the case of off-resonant scattering $|\omega_{ext} - \omega_\sigma| \gg \gamma_\sigma$. As a result, in the denominators of Eqs. (12.2.19) and (12.2.20), we can neglect $\Omega_{R\,pl}^2$ compared to $|(-i(\omega_{ext} - \omega_\sigma) + \gamma_\sigma)(-i(\omega_{ext} - \omega_{pl}) + \gamma_{pl})| \sim (\omega_{ext} - \omega_\sigma)\gamma_{pl}$ (see Eq. (12.2.8)). Thanks to inequalities (12.2.8), in the numerator of Eq. (12.2.20), we can also neglect $\Omega_{R\,pl}$ in comparison with $\alpha(i(\omega_{ext} - \omega_\sigma) + \gamma_\sigma)$.

The strong coupling regime implies that the Rabi constant of the interaction between the PNA and the TLS is large, $\alpha\Omega_{R\,pl} \gg |\omega_{ext} - \omega_{pl}|, \gamma_{pl}$. Therefore, in the numerator of Eq. (12.2.19), we neglect $(-i(\omega_{ext} - \omega_{pl}) + \gamma_{pl})$ compared with $\alpha\Omega_R$. After these simplifications, we obtain the following expression for the Rayleigh amplitudes:

$$\widehat{\sigma}_1 = S_{SERS}e^{-i\omega_{ext}t}\widehat{I}, \tag{12.2.22}$$

$$\widehat{a}_1 = \Upsilon_{SERS}e^{-i\omega_{ext}t}\widehat{I}. \tag{12.2.23}$$

Here

$$S_{SERS} \approx \frac{1}{2}\frac{\Omega_{R\,pl}}{\omega_{ext} - \omega_\sigma}\frac{\alpha\Omega_{ext}}{\omega_{ext} - \omega_{pl} + i\gamma_{pl}} = \frac{\Omega_{R\,pl}}{\omega_{ext} - \omega_\sigma}\Upsilon_{SERS} \tag{12.2.24}$$

$$\Upsilon_{SERS} = \frac{\alpha\Omega_{ext}}{2\left(\omega_{ext} - \omega_{pl} + i\gamma_{pl}\right)}. \tag{12.2.25}$$

According to Eq. (11.1.31) for spontaneous Raman scattering, the factor $S = \Omega_{ext}/2(\omega_{ext} - \omega_\sigma)$ gives the amplitude of Rayleigh scattering in the absence of the PNA; therefore, S_{SERS} is the factor responsible for the field enhancement due to the plasmonic resonance. According to Eq. (12.1.15), $\alpha \approx (d_{pl}/d_{\mathrm{eg}})$, then S_{SERS}/S may be rewritten as

$$\frac{S_{SERS}}{S} = \frac{d_{pl}E/\hbar}{\omega_{ext} - \omega_{pl} + i\gamma_{pl}}.$$

The greatest enhancement is achieved at $|\omega_{ext} - \omega_{pl}| \ll \gamma_{pl}$. In such a case, the Purcell factor is simplified (see Eq. (12.1.30)):

$$F_{\mathrm{P}} = \frac{\gamma_{res}}{\gamma_\sigma} = 1 + \frac{\Omega_{R\,pl}^2}{\gamma_{pl}\gamma_\sigma} \sim \frac{\Omega_{R\,pl}^2}{\gamma_{pl}\gamma_\sigma},$$

and we can express the SERS enhancement through the Purcell factor as

$$S_{SERS}/S \simeq \alpha\big(-i\Omega_{R\,pl}\big)/\gamma_{pl} = \big(-i\Omega_{R\,pl}\big)/\sqrt{\gamma_{pl}\gamma_\sigma} \simeq -i\sqrt{F_p} \tag{12.2.26}$$

$$\Upsilon_{SERS} = (S_{SERS}/S)\Omega_{ext}/\Omega_{R\,pl} \sim -\kappa\big(\mathbf{d}_{eg}\cdot\mathbf{E}_{ext}/\big|\mathbf{d}_{eg}\big|\big) \sim i\sqrt{F_P}E_{ext} \tag{12.2.27}$$

Here, we have assumed that the enhancement is large ($\kappa \gg 1$) and have used $\alpha = \sqrt{\gamma_{pl}/\gamma_\sigma}$ (see Eq. (12.1.15)). Thus, we obtain that the expectation value $\langle\widehat{\sigma}_1\rangle$ increases as the square root of the Purcell factor (see also Ref. [11]). Below, we show that the enhancement Υ_{SERS} is only a part of the contribution to the increase in the Raman peaks. To calculate the Raman spectrum, we have to consider the next order of the perturbation theory. We obtain the following two equations:

$$d\widehat{\sigma}_2/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_2 = -i\omega_{\mathrm{pl}}\widehat{a}_{pl\,2} - ig\widehat{\sigma}_1\int_0^t\Big[e^{i\omega_v(t-t')}\widehat{F}_b^\dagger(t') + e^{-i\omega_v(t-t')}\widehat{F}_b(t')\Big]dt', \tag{12.2.28}$$

$$d\widehat{a}_{pl\,2}/dt + \big(i\omega_{pl} + \gamma_{pl}\big)\widehat{a}_{pl\,2} = -i\Omega_{R\,pl}\widehat{\sigma}_2. \tag{12.2.29}$$

The particular solution to Eq. (12.2.28) can be written as (Problem 2.3)

$$\begin{aligned}\sigma_2(t) = -igS_{SERS}e^{-(i\omega_\sigma+\gamma_\sigma)t}\Bigg[&\int_0^t d\tau e^{(-i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau}e^{(i\omega_v-\gamma_v)\tau}\int_0^\tau d\tau' e^{(-i\omega_v+\gamma_v)\tau'}\widehat{F}_b^\dagger(\tau')\\ &-\int_0^t d\tau e^{(-i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau}e^{(-i\omega_v-\gamma_v)\tau}\int_0^\tau d\tau' e^{(i\omega_v+\gamma_v)\tau'}\widehat{F}_b(\tau')\Bigg].\end{aligned} \tag{12.2.30}$$

The particular solution to Eq. (12.2.29) is

$$a_2(t) = -i\Omega_{Rpl}\int_0^t d\tau e^{\left(i\omega_{pl}-\gamma_{pl}\right)(t-\tau)}\sigma_2(\tau). \tag{12.2.31}$$

Assuming that the main source of the Raman signal is the PNA, we find the scattering spectrum. To achieve this, as discussed in Sect. 3.4.1 of Part I, it is sufficient to calculate the correlator:

$$\left\langle \widehat{a}^{\dagger}_{pl}(t+\tau)\widehat{a}_{pl}(t)\right\rangle = \left\langle \widehat{a}^{\dagger}_{pl\,1}(t+\tau)\widehat{a}_{pl\,1}(t)\right\rangle + \left\langle \widehat{a}^{\dagger}_{pl\,2}(t+\tau)\widehat{a}_{pl\,2}(t)\right\rangle \tag{12.2.32}$$

We neglect $\langle a^{\dagger}{}_1 a_2\rangle$ because, according to Eq. (12.2.23), $\widehat{a}_1 = \Upsilon_{SERS}e^{-i\omega_{ext}t}\widehat{I}$, and therefore, $\left\langle a^{\dagger}{}_1 a_2\right\rangle \sim \Upsilon_{SERS}e^{i\omega_{ext}t}\langle a_2\rangle \sim \langle F_b\rangle = 0$. To calculate two-time correlator (12.2.32), we use Eqs. (12.2.30) and (12.2.31), and noise properties (11.1.6)–(11.1.10). As a result, we obtain (see Problem 2.3):

$$\begin{aligned}
&\left\langle \widehat{a}^{\dagger}(t+\tau)\widehat{a}(t)\right\rangle \\
&\quad = \left\langle \widehat{a}^{\dagger}_1(t+\tau)\widehat{a}_1(t)\right\rangle + \left\langle \widehat{a}^{\dagger}_2(t+\tau)\widehat{a}_2(t)\right\rangle \\
&\quad = |\Upsilon_{SERS}|^2 e^{i\omega_{ext}\tau} + \left[A_{pSt}(1+n_v(T))e^{\left(i(\omega_{ext}-\omega_v)-\frac{\gamma_v}{2}\right)\tau} + A_{paSt}n_v(T)e^{\left(i(\omega_{ext}+\omega_v)-\frac{\gamma_v}{2}\right)\tau}\right]
\end{aligned} \tag{12.2.33}$$

where

$$A_{pSt}(\omega) = |S_{SERS}|^2\left[\frac{g^2}{\left(\omega_\sigma-\omega+\omega_v\right)^2+\gamma_\sigma^2}\right]\left[\frac{\Omega_{Rpl}^2}{\left(\omega_{pl}-\omega+\omega_v\right)^2+\gamma_a^2}\right] \tag{12.2.34}$$

$$A_{paSt}(\omega) = |S_{SERS}|^2\left[\frac{g^2}{\left(\omega_\sigma-\omega_{ext}-\omega_v\right)^2+\gamma_\sigma^2}\right]\left[\frac{\Omega_{Rpl}^2}{\left(\omega_{ext}-\omega_{pl}+\omega_v\right)^2+\gamma_{pl}^2}\right] \tag{12.2.35}$$

where we assumed that the frequency of the external field ω_{ext} is sufficiently far from the resonance of the TLS so that the conditions $\gamma_{pl}|\omega_\sigma-\omega_{ext}| \gg \Omega_{Rpl}^2$ and $|\omega_\sigma - \omega_{ext} \pm \omega_v| \gg \gamma_\sigma$ are satisfied; $|S_{SERS}|^2$ is defined by Eq. (12.2.24). The spectrum described by Eq. (12.2.33) contains three peaks corresponding to the Stokes signal on the frequency $\omega_{ext} - \omega_v$, the Rayleigh signal on the frequency ω_{ext}, and the anti-Stokes signal on the frequency $\omega_{ext} + \omega_v$.

To obtain the radiation spectrum of SERS, we should make the Fourier transform of Eq. (12.2.33), arriving at the spectrum of oscillation of the dipole moment (see Eq. (3.4.52)), and multiply it by $2(\omega_{ext}-\omega_v)^4|\mathbf{d}_{pl}|^2/3c^3$:

$$I_{SERS}(\omega) = \frac{2(\omega_{ext}-\omega_v)^4}{3c^3}|\mathbf{d}_{pl}|^2 \,\mathrm{Re}\int_0^{+\infty}\left\langle \hat{a}^\dagger(t+\tau)\hat{a}(t)\right\rangle e^{-i\omega'\tau}d\tau$$
$$= \frac{2\omega_{ext}^4}{3c^3}|\mathbf{d}_{eg}|^2\alpha^2|\Upsilon_{SERS}|^2\delta(\omega-\omega_{ext}) + \frac{2(\omega_{ext}-\omega_v)^4|\mathbf{d}_{eg}|^2}{3c^3}\frac{\alpha^2 A_{pS}(1+n_v(\omega_v,T))\gamma_v}{(\omega_{ext}-\omega_v-\omega)^2+(\gamma_v/2)^2}$$
$$+\frac{2(\omega_{ext}+\omega_v)^4|\mathbf{d}_{eg}|^2}{3c^3}\frac{\alpha^2 A_{paS} n_v(\omega_v,T)\gamma_v}{(\omega_{ext}+\omega_v-\omega)^2+(\gamma_v/2)^2}. \tag{12.2.36}$$

This spectrum has one δ-function-shaped term responsible for the Rayleigh scattering and two terms with the Lorentzian profiles responsible for the Stokes $A_{pS}(\omega)$ and anti-Stokes $A_{apS}(\omega)$ signals. The Raman contributions to the spectrum have a width equal to the damping rate of the nuclear oscillations and are, therefore, incoherent contributions to the spectrum.

According to Eqs. (12.2.36) and (11.1.45), under the conditions $\gamma_a|\omega_\sigma-\omega_{ext}| \gg \omega_{pl}^2$ and $|\omega_\sigma-\omega_{ext}\pm\omega_v| \gg \gamma_\sigma$, the ratio of intensities of the Stokes component in SERS and spontaneous Raman scattering is

$$\frac{I_{pl}(\omega_{St})}{I_\sigma(\omega_{St})} = \frac{|S_{SERS}|^2}{|S|^2}\frac{\alpha^2\Omega_{R\,pl}^2}{(\omega_{ext}-\omega_{pl}-\omega_v)^2+\gamma_{pl}^2}$$
$$= \frac{\alpha^2\Omega_{R\,pl}^2}{(\omega_{ext}-\omega_{pl})^2+\gamma_{pl}^2}\cdot\frac{\alpha^2\Omega_{R\,pl}^2}{(\omega_{ext}-\omega_{pl}-\omega_v)^2+\gamma_{pl}^2}. \tag{12.2.37}$$

The first factor on the right-hand side of this equation is the amplification of the local electric field exerted on the molecule. The second factor appears due to the Purcell effect and is responsible for the faster emission of the spontaneous Raman signal from the molecule.

Thus, the enhancement of the light scattered by a molecule includes contributions from two physical processes.

First, at the plasmonic resonance $\omega_{ext} \approx \omega_{pl}$, the near-field of the nanoparticle is enhanced. The amplitude of the molecular dipole moment oscillation is increased proportionally to the enhancement of the local field. As was shown, the effect results in the first Purcell factor in Eq. (12.2.38).

Second, in typical SERS experiments, the dipole moment of a plasmon nanoparticle exceeds the dipole moment of the electron transition in a molecule by several orders of magnitude; consequently, the contribution of the nanoparticle into the scattered light significantly exceeds the contribution of the molecule $\alpha = d_{pl}/d_{\mathrm{eg}} \gg 1$.

Due to the Purcell effect, the near-field energy transfer to the plasmon nanoparticle is faster than the energy emission of the molecule into empty space. At the Stokes frequency, the plasmon is fed by the excited molecule. This process is responsible for the second Purcell factor in Eq. (12.2.38).

Thus, the light scattering on the molecule also effectively increases in the presence of the plasmon nanoparticle.

Taking into account that the ratio $\alpha = d_{pl}/d_{\mathrm{eg}}$ is much greater than unity, we obtain the following estimate for the case of a high Purcell factor: $F_{\mathrm{P}} \simeq \Omega_{R\,pl}^2 \alpha^2 / \gamma_{pl}^2$. From Eq. (12.2.37) we obtain that the maximum amplification of the Stokes signal in the SERS effect is achieved when $\omega_{ext} - \omega_{pl} \approx \omega_v$; in this case, $\omega_{St} = \omega_{ext} - \omega_v \approx \omega_{pl}$

$$\frac{I_{SERS}(\omega_{St})}{I(\omega_{St})} = \frac{\alpha^2 \Omega_{R\,pl}^2}{\gamma_a^2} \cdot \frac{\alpha^2 \Omega_{R\,pl}^2}{\gamma_a^2} \approx F_P^2 \gg 1 \tag{12.2.38}$$

To conclude, if a molecule is placed near a plasmonic nanoantenna, the enhancement of spontaneous Raman scattering turns out to be linear in the incident intensity and is proportional to the fourth power in the coupling constant of the plasmon with the molecule. Numerically, the coefficient of the enhancement is equal to the Purcell factor squared. In terms of antenna theory, the PNA acts as a mediator that improves the connection (impedance) between the TLS and EM modes of free surrounding space.

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Chapter 13
The Progress in Study of the Raman Effect After the Laser Invention

The invention of lasers provided a new tool for studying the optical properties of materials. In particular, it becomes possible to observe many new nonlinear effects, for example, wave mixing and generation of the higher harmonics [1, 2]. That led to the development of a new branch of optics—nonlinear optics [3], which successfully describes coherent and high-intensity laser radiation. In Raman spectroscopy, the employment of nonlinear optics simplifies the consideration of coherent phenomena.

Before the invention of lasers, spectroscopists had little interest in the degree of coherence of the spectra under study, which was justified by the fact that they were dealing with incoherent light sources. Moreover, spontaneous Raman scattering remains incoherent regardless of the power or coherence of the incident wave.

The advent of lasers has revolutionized Raman spectroscopy essentially by making the Raman scattering coherent. Indeed, new phenomena observed in the Raman scattering of laser radiation, such as SRS, Raman amplification, and CARS, arise due to the coherence of light.

To observe the coherent Raman scattering, one needs two coherent incident waves with slightly different frequencies. In this case, the total EM field exhibits beats. The total field can be presented as a carrying wave with the mean frequency. The amplitude of the carrying wave is modulated by the beat frequency, which is equal to the difference between frequencies of the incident waves. However, in the description of linear oscillations, the beat frequency does not manifest itself in the spectrum of the field oscillations. The spectrum consists of only two frequencies of the incident waves. We, therefore, cannot excite a resonator whose eigenfrequency is equal to the beat frequency. The situation changes dramatically if we consider the nonlinear oscillations.

It is the nonlinearity of the interaction between the electronic and vibronic subsystems of the molecule that results in the appearance of the beat frequency in the spectrum of the Fröhlich force. If the beat frequency coincides with the eigenfrequency of nuclei oscillations, the resonant excitation of coherent vibrons occurs, making it possible to obtain a coherent Raman response. To observe a markedly coherent Raman response, the vibration of nuclei should exhibit a high

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Q-factor. Thus, the high-Q resonant excitation of vibrons brings a new parameter $\gamma_v \ll \omega_v$ into the problem. Thus, since $g \sim \omega_v \gg \gamma_v$, we cannot consider the Fröhlich coupling constant to be a small parameter.

In this chapter, we consider both Raman amplification, including Raman lasing, and collective phenomena like CARS.

13.1 The Spectrum of Nonlinear Coherent Response of a Raman-Active Molecule on Two Monochromatic Electromagnetic Waves

In this section, the object of the study is a molecule illuminated by two coherent signals having frequencies ω_S (the signal beam) and ω_P (the pumping beam) with ω_S, $\omega_P < \omega_\sigma$. We base our consideration on Hamiltonian (10.1.23), to which we add the second external monochromatic field.

As before, we model the electronic part of the molecule by a TLS and use the rotating wave approximation. The system Hamiltonian has the following form:

$$\widehat{H}_S = \hbar\omega_\sigma \widehat{\sigma}^\dagger \widehat{\sigma} + \hbar\omega_v \widehat{b}^\dagger \widehat{b} + \hbar g \widehat{\sigma}^\dagger \widehat{\sigma}\left(\widehat{b}^\dagger + \widehat{b}\right) + \frac{\hbar\Omega_P}{2}\left(\widehat{\sigma}^\dagger e^{-i\omega_P t} + \widehat{\sigma} e^{i\omega_P t}\right) + \frac{\hbar\Omega_S}{2}\left(\widehat{\sigma}^\dagger e^{-i\omega_S t} + \widehat{\sigma} e^{i\omega_S t}\right). \tag{13.1.1}$$

The last two terms of Eq. (13.1.1) are responsible for the interactions of the TLS and two external harmonic fields with the frequencies ω_P and ω_S. The corresponding Rabi constants are $\Omega_P = -\mathbf{d}_{eg} \cdot \mathbf{E}_P/\hbar$ and $\Omega_S = -\mathbf{d}_{eg} \cdot \mathbf{E}_S/\hbar$, where $\mathbf{E}_P \sim \mathbf{E}_S$ are the amplitudes of the electric fields of the respective incident signals, and, as before, $\mathbf{d}_{eg}$ is the dipole moment of the TLS transition. Hereinafter, for certainty, we assume that $\omega_S < \omega_P$. We confine ourselves to considering Raman-active molecules, assuming that the dipole moment of the transition between the vibrational levels is zero, so the external electric field directly affects only the electronic subsystem of the molecule.

From Hamiltonian (13.1.1), one can obtain the system of the Heisenberg-Langevin equations for the operator of the nuclear vibrations $\widehat{b}$ and the TLS operator $\widehat{\sigma}$:

$$d\widehat{b}/dt + (i\omega_v + \gamma_v)\widehat{b} = -ig\widehat{\sigma}^\dagger \widehat{\sigma} + \widehat{F}_b(t), \tag{13.1.2}$$

$$d\widehat{\sigma}/dt = (-i\omega_\sigma - \gamma_\sigma)\widehat{\sigma} + \frac{i}{2}\left(2\widehat{\sigma}^\dagger \widehat{\sigma} - 1\right)\left(\Omega_P e^{-i\omega_1 t} + \Omega_S e^{-i\omega_2 t}\right) - ig\widehat{\sigma}\left(\widehat{b}^\dagger + \widehat{b}\right). \tag{13.1.3}$$

where γ_v and γ_σ are the relaxation rates of the nuclear vibrations and TLS excitations, respectively. Note that Eq. (13.1.2) is identical to Eq. (11.1.5), while Eq. (13.1.3) differs from Eq. (11.1.4) because it has an additional term due to the second external field. This term causes a qualitative change in the behavior of the system.

Note that in the absence of the interaction between the electronic and vibronic subsystems, the response of a small dipole moment $\widehat{\sigma}$ is close to the sum of the responses on each wave. Since $\omega_\sigma > \omega_S, \omega_P$, the dipole moments are small. It may seem that accounting for a small interaction is unlikely to lead to a strong change in these responses.

Nevertheless, the Fröhlich Hamiltonian gives a harmonic time dependence with the beat frequency $\omega_B = \omega_P - \omega_S$. Thus, the second incident wave introduces a new characteristic frequency into the problem—the beat frequency ω_B. If $\omega_B = \omega_v$, there appears a resonant enhancement of nuclei vibration that dramatically increases the Raman response.

We do not know the exact solution to Eqs. (13.1.2) and (13.1.3); therefore, we use the perturbation theory to confirm the above-suggested hypothesis that the excitation of a coherent response is connected with the appearance of the beat frequency in the spectrum of effective force driving the vibrons. To construct such a theory, we take advantage of the smallness of Ω_P and Ω_S compared to characteristic frequencies of the system. Thus, small dimensionless parameters can be introduced:

$$\Omega_P/\omega_\sigma \ll 1, \quad \Omega_S/\omega_\sigma \ll 1, \quad g/\omega_\sigma \ll 1 \tag{13.1.4}$$

while $g \sim \omega_v$. Since we are looking for a pronounced effect, we assume that the quality factor of vibrons is high, i.e., $Q_v = \omega_v/\gamma_v \sim g/\gamma_v$ is large. This means that the mean number of excited vibrons may be greater than unity. Below, we assume that $Q_v > \omega_\sigma/\omega_v$ or

$$(g/\gamma_v) \geq (\omega_\sigma/g). \tag{13.1.5}$$

Based on inequalities (13.1.4) and that $\Omega_P \sim \Omega_S$, we can introduce a small perturbation parameter:

$$\varepsilon \sim \Omega_P/\omega_\sigma \sim \Omega_S/\omega_\sigma. \tag{13.1.6}$$

We seek a solution to the set of Eqs. (13.1.2) and (13.1.3) in the form of expansions (12.2.9). Note that to neglect the noises in the electronic subsystem, we need to maintain inequality (13.1.4) for both external waves.

In the zeroth order of the perturbation theory, the results are the same as given by Eqs. (11.1.26) and (11.1.23):

$$\widehat{b}_0(t) = \int_0^t \exp((-i\omega_v - \gamma_v)(t-t'))\widehat{F}_b(t')dt' \tag{13.1.7}$$

$$\widehat{\sigma}_0 = 0 \tag{13.1.8}$$

where $\widehat{b}_0(t)$ is determined by incoherent thermal nuclear vibrations arising due to the molecule interaction with the environment. The average number of nuclear vibrations is determined by the Bose-Einstein distribution Eq. (11.1.27).

When using Eq. (11.1.27), we assume that time $t \gg \gamma_v^{-1}$ so that the nuclear system is in thermal equilibrium. Therefore, in the zeroth order, we have an incoherent response of the vibrating nuclear subsystem and a zero response of the electronic subsystem.

In the first order of the perturbation theory, Eqs. (13.1.2) and (13.1.3) are modified:

$$d\widehat{b}_1/dt + (i\omega_v + \gamma_v)\widehat{b}_1 = 0, \tag{13.1.9}$$

$$d\widehat{\sigma}_1/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_1 = -\frac{i}{2}\left(\Omega_P e^{-i\omega_P t} + \Omega_S e^{-i\omega_S t}\right)\widehat{I}. \tag{13.1.10}$$

For $t \gg \gamma_v^{-1}$, the steady-state solutions to these equations are

$$\widehat{b}_1 = 0 \tag{13.1.11}$$

$$\widehat{\sigma}_1 = \frac{1}{2}\left(\frac{\Omega_S}{\omega_S - \omega_\sigma + i\gamma_\sigma}e^{-i\omega_S t} + \frac{\Omega_P}{\omega_P - \omega_\sigma + i\gamma_\sigma}e^{-i\omega_P t}\right)\widehat{I}. \tag{13.1.12}$$

Thus, in the first order, there is still no correction to the response of the nuclear subsystem. It is still unaffected by the EM field, while the electronic subsystem exhibits the linear coherent response on the external field. This confirms our earlier assumption that $\widehat{\sigma}$ is close to the sum of the responses on each wave. Consequently, in the second order, on the right-hand side of equations, a source oscillating at the beat frequency should appear. Indeed,

$$d\widehat{b}_2/dt + (i\omega_v + \gamma_v)\widehat{b}_2 = -ig\widehat{\sigma}_1^\dagger\widehat{\sigma}_1, \tag{13.1.13}$$

$$d\widehat{\sigma}_2/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_2 = -ig\widehat{\sigma}_1\left(\widehat{b}_0^\dagger + \widehat{b}_0\right). \tag{13.1.14}$$

Substituting Eq. (13.1.12) into Eq. (13.1.13), we can see that due to the nonlinearity of the right-hand side of Eq. (13.1.13), the beat frequency $\omega_B = \omega_S - \omega_P$ appears as a new characteristic frequency for vibrons. This leads to the resonance response of $\widehat{b}_2$.

One can obtain the solutions to Eqs. (13.1.13) and (13.1.14) by substituting the expressions for $\widehat{\sigma}_1$ (Eq. (13.1.12)) and $\widehat{b}_0$ (Eq. (13.1.7)) into these equations[1] (see Problem 2.4):

[1] To obtain Eqs. (13.1.15) and (13.1.16), we substitute the expressions for $\widehat{\sigma}_1$ (see Eq. (13.1.12)) and $\widehat{b}_0$ into Eq. (1.4) of Problem 2.1.

$$\begin{aligned}\widehat{b}_2 \approx \Bigg(&\frac{1}{4}\frac{\Omega_S^*\Omega_P}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}\cdot\frac{g}{\omega_B-\omega_v+i\gamma_v}e^{-i\omega_B t}\\ &+\frac{1}{4}\frac{\Omega_P^*\Omega_S}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}\cdot\frac{g}{\omega_B+\omega_v+i\gamma_v}e^{i\omega_B t}\\ &+\frac{1}{4}\frac{|\Omega_S|^2}{(\omega_\sigma-\omega_S)^2}\cdot\frac{g}{-\omega_v+i\gamma_v}+\frac{1}{4}\frac{|\Omega_P|^2}{(\omega_\sigma-\omega_P)^2}\cdot\frac{g}{-\omega_v+i\gamma_v}\Bigg)\widehat{I},\end{aligned} \tag{13.1.15}$$

$$\begin{aligned}\widehat{\sigma}_2(t) =& -ige^{-(i\omega_\sigma+\gamma_\sigma)t}\int_0^t dt' \mathrm{e}^{(i\omega_\sigma+\gamma_\sigma)t'}\left(\frac{\Omega_S e^{-i\omega_S t}}{\omega_S-\omega_\sigma+i\gamma_\sigma}+\frac{\Omega_P e^{-i\omega_P t}}{\omega_P-\omega_\sigma+i\gamma_\sigma}\right)\\ &\times\int_0^{t'} dt'' e^{-\gamma_v(t'-t'')}\left[e^{i\omega_v(t'-t'')}\widehat{F}_b^\dagger(t'')+e^{-i\omega_v(t'-t'')}\widehat{F}_b(t'')\right].\end{aligned} \tag{13.1.16}$$

We can see that when a harmonic source is added to the right-hand side of the vibron dynamics equation, the Fröhlich Hamiltonian causes the resonance excitation of vibrons if $\omega_B = \omega_v$.

In this order of the perturbation theory, we can see that the incidence of two coherent waves causes an excitation of coherent oscillation of the nuclear subsystem and an incoherent oscillation of the electronic subsystem. The coherent oscillation of the nuclear subsystem is generated on the beat frequency $\omega_B = \omega_P - \omega_S$, while the incoherent response of the electronic subsystem contains terms on the six carrier frequencies, namely, on the Rayleigh frequencies ω_P and ω_S and on the Raman frequencies $\omega_S \pm \omega_B$ and $\omega_P \pm \omega_B$.

The coherent Raman scattering is exhibited in the third order of the perturbation theory for $\widehat{\sigma}$:

$$d\widehat{\sigma}_3/dt + (i\omega_\sigma+\gamma_\sigma)\widehat{\sigma}_3 = -ig\widehat{\sigma}_1\left(\widehat{b}_2^\dagger+\widehat{b}_2\right)+i\widehat{\sigma}_1^\dagger\widehat{\sigma}_1\left(\Omega_S e^{-i\omega_S t}+i\Omega_P e^{-i\omega_P t}\right), \tag{13.1.17}$$

Note that all operators on the right-hand side of Eq. (13.1.17) cause coherent responses $\langle\widehat{\sigma}_3\rangle$.

In the equation for $\widehat{\sigma}_3$, the nonlinear term $-ig\widehat{\sigma}_1\left(\widehat{b}_2^\dagger+\widehat{b}_2\right)$ appears due to the TLS interaction with the nuclear subsystem, while the nonlinear term $i\widehat{\sigma}_1^\dagger\widehat{\sigma}_1(\Omega_S e^{-i\omega_S t}+i\Omega_P e^{-i\omega_P t})$ comes from the saturation of the TLS population

inversion under the action of the external fields (recall that population inversion is $D_1 = 2\widehat{\sigma}_1^{\dagger}\widehat{\sigma}_1 - 1$). Both nonlinearities contain terms oscillating on four frequencies ω_P, ω_S, $2\omega_P - \omega_S = \omega_P + \omega_B$, and $2\omega_S - \omega_P = \omega_S - \omega_B$. The latter two frequencies correspond to CARS and coherent Stokes Raman scattering (CSRS).

Taking into account the explicit expressions for $\widehat{\sigma}_1$, $\widehat{\sigma}_1^{\dagger}$, $\widehat{b}_2^{\dagger}$, and $\widehat{b}_2$, Eq. (13.1.17) can be rewritten in the following form (see Problem 2.4):

$$\begin{aligned} d\widehat{\sigma}_3/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_3 = \widehat{I}\Big[&\left(S_{\omega_P} + S_{\omega_P}^{(g)}\right)e^{-i\omega_P t} + \left(S_{\omega_S} + S_{\omega_S}^{(g)}\right)e^{-i\omega_S t} \\ &+ \left(S_{2\omega_S-\omega_P} + S_{2\omega_S-\omega_P}^{(g)}\right)e^{-i(2\omega_S-\omega_P)t} \\ &+ \left(S_{2\omega_P-\omega_S} + S_{2\omega_P-\omega_S}^{(g)}\right)e^{-i(2\omega_P-\omega_S)t}\Big], \end{aligned} \tag{13.1.18}$$

where

$$\begin{aligned} S_{\omega_P} &= \frac{i|\Omega_S|^2\Omega_P}{4(\omega_S-\omega_\sigma)^2} + \frac{i|\Omega_P|^2\Omega_P}{4(\omega_P-\omega_\sigma)^2} + \frac{i|\Omega_S|^2\Omega_P}{4(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}, \\ S_{\omega_S} &= \frac{i|\Omega_S|^2\Omega_S}{4(\omega_S-\omega_\sigma)^2} + \frac{i|\Omega_P|^2\Omega_S}{4(\omega_P-\omega_\sigma)^2} + \frac{i|\Omega_P|^2\Omega_S}{4(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}, \\ S_{2\omega_S-\omega_P} &= \frac{i\Omega_P^*\Omega_S^2}{4(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}, \\ S_{2\omega_P-\omega_S} &= \frac{i\Omega_S^*\Omega_P^2}{4(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)} \end{aligned} \tag{13.1.19}$$

are the nonlinear responses independent of the Fröhlich interaction; they oscillate with the frequencies ω_P, ω_S, $2\omega_S - \omega_P$, and $2\omega_P - \omega_S$. These responses arise due to the TLS saturation. The subscripts at the nonlinear responses S indicate the frequencies with which the respective terms oscillate. The factors in the denominators, like $(\omega_\sigma - \omega_S)$ and $(\omega_\sigma - \omega_P)$, indicate the connection of the nonlinear response with the saturation of the excited electronic state. The resonances appear if $\omega_S = \omega_\sigma$ or $\omega_P = \omega_\sigma$. The saturation is observed if we take into account the radiation rate γ_σ, which is omitted because $\gamma_\sigma \ll |\omega_\sigma - \omega_S|$. Note that the beat frequency does not appear in any expression (13.1.19).

The terms $S^{(g)}$ in Eq. (13.1.18) arise due to the nonlinearity caused by the Fröhlich interaction between electronic and nuclear degrees of freedom:

$$
\begin{aligned}
S_{\omega_S}^{(g)} &= \frac{-ig^2|\Omega_P|^2\Omega_S}{8(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)^2} \\
&\times\left(\frac{(\omega_\sigma-\omega_P)^2}{(\omega_\sigma-\omega_S)^2}\cdot\frac{2\omega_v}{\omega_v^2+\gamma_v^2}+\frac{2\omega_v}{\omega_v^2+\gamma_v^2}+\frac{1}{\omega_B+\omega_\nu-i\gamma_\nu}-\frac{1}{\omega_B-\omega_\nu-i\gamma_\nu}\right), \\
S_{\omega_P}^{(g)} &= \frac{-ig^2|\Omega_S|^2\Omega_P}{8(\omega_\sigma-\omega_S)^2(\omega_\sigma-\omega_P)} \\
&\times\left(\frac{(\omega_\sigma-\omega_S)^2}{(\omega_\sigma-\omega_P)^2}\cdot\frac{2\omega_v}{\omega_v^2+\gamma_v^2}+\frac{2\omega_v}{\omega_v^2+\gamma_v^2}+\frac{1}{\omega_B+\omega_\nu+i\gamma_\nu}-\frac{1}{\omega_B-\omega_\nu+i\gamma_\nu}\right), \\
S_{2\omega_S-\omega_P}^{(g)} &= \frac{-ig^2\Omega_P^*\Omega_S^2}{8(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)(\omega_S-\omega_\sigma)(\omega_P-\omega_S-\omega_\nu-i\gamma_\nu)} \\
&+\frac{-ig^2\Omega_P^*\Omega_S^2}{8(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)(\omega_S-\omega_\sigma)(\omega_S-\omega_P-\omega_\nu+i\gamma_\nu)}, \\
S_{2\omega_P-\omega_S}^{(g)} &= -\frac{-ig^2\Omega_S^*\Omega_P^2}{8(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)(\omega_P-\omega_\sigma)(\omega_P-\omega_S-\omega_\nu+i\gamma_\nu)} \\
&+\frac{-ig^2\Omega_S^*\Omega_P^2}{8(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)(\omega_P-\omega_\sigma)(\omega_S-\omega_P-\omega_\nu-i\gamma_\nu)}
\end{aligned}
\tag{13.1.20}
$$

The resonance appears if $\omega_B = \omega_v$ and is connected with resonant excitation of the vibrons (see Eq. (13.1.15)).

Let us discuss the smallness of the contributions to σ_3 due to various terms on the right-hand side of Eq. (13.1.18). The contributions of the terms that do not depend on g (Eq. (13.1.19)) are of the order $\widehat{\sigma}_3 \sim \varepsilon^3 \sim \Omega_{S,P}^3/\omega_\sigma^3$. In experiment, one should use $\omega_B \sim \omega_v$; consequently, we obtain that contributions of the terms that depend on g (see Eq. (13.1.20)) are of the order $\sim \Omega_{S,P}^3 g^2/\omega_\sigma^4\gamma_v \sim \left(\Omega_{S,P}^3/\omega_\sigma^3\right)(g^2/\omega_\sigma\gamma_v)$. Thus, all terms in Eqs. (13.1.19) and (13.1.20) are of the same order because we suppose that $g^2/\omega_\sigma\gamma_v \sim (g/\gamma_v)(g/\omega_\sigma) \sim 1$ (see Eq. (13.1.5)).

Thus, the steady-state solution of Eq. (13.1.18) consists of terms oscillating with the frequencies ω_S, ω_P, $2\omega_S - \omega_p$, and $2\omega_P - \omega_S$. Due to the linearity of Eq. (13.1.18), the stationary solution to Eq. (13.1.18) may be sought as the sum of terms oscillating with the same frequencies:

$$
\widehat{\sigma}_3 = \widehat{\sigma}_3^{(\omega_S)} + \widehat{\sigma}_3^{(\omega_P)} + \widehat{\sigma}_3^{\left(2\omega_S-\omega_p\right)} + \widehat{\sigma}_3^{(2\omega_P-\omega_S)} + \widehat{\sigma}_3^{(g,\omega_S)} + \widehat{\sigma}_3^{\left(g,\omega_p\right)} + \widehat{\sigma}_3^{(g,2\omega_S-\omega_P)} + \widehat{\sigma}_3^{(g,2\omega_S-\omega_P)}
\tag{13.1.21}
$$

For convenience, in Eq. (13.1.21), we separate the terms dependent and independent of the Fröhlich constant g.

The g-independent terms are significant if $|\omega_P - \omega_\sigma|, |\omega_S - \omega_\sigma| \ll \gamma_\sigma$. This means that although ω_P, $\omega_S \sim \omega_\sigma$, the Lorentzian lines corresponding to these frequencies can be resolved. The other terms exhibit resonance at

$$\omega_P - \omega_S = \omega_B = \omega_v; \tag{13.1.22}$$

this resonance arises due to the Fröhlich interaction (10.1.20) between electronic and nuclear degrees of freedom. In terms of nonlinear optics, this interaction mixes four waves [4] with frequencies ω_P, ω_S, $2\omega_S - \omega_P$, and $2\omega_P - \omega_S$. The terms depending on g can be considered as an implicit interaction of the pump and signal waves, resulting in the generation of these waves. Below, we show that each of these terms is responsible for its own specific phenomenon, such as Raman amplification, SRS, or CARS.

When relationship (13.1.22) is satisfied, the frequency $2\omega_S - \omega_P$ becomes the Stokes frequency for Raman scattering of the signal wave:

$$2\omega_S - \omega_P = \omega_S - \omega_v, \tag{13.1.23}$$

while the frequency $2\omega_P - \omega_S$ corresponds to the anti-Stokes frequency for Raman scattering of the pumping wave:

$$2\omega_P - \omega_S = \omega_P + \omega_v \tag{13.1.24}$$

13.2 The Raman Amplification (Semiclassical Approach)

The Raman amplification is observed when two classical (coherent) waves propagate through a medium of the Raman-active molecules. This amplification occurs due to the nonlinear interaction of two coherent light waves traveling in the same direction. The waves interact via Raman-active molecules. One of the waves is referred to as a signal wave with the frequency ω_S, and it is assumed that this wave is weak and requires amplification. The second is the high-power pump wave with the frequency ω_P [5]. The maximum amplification of the signal wave is observed at vibron resonance when the wave frequencies satisfy Eq. (13.1.22). In this case, the signal wave is amplified by receiving the energy from the pump wave. Thanks to relationship (13.1.22), the signal wave is often called the Stokes wave.

13.2.1 Mechanism of Energy Transfer from One Wave to the Other

In this section, we consider the energy exchange between two waves traveling in a Raman-active medium. We show that the pump wave transfers energy to a molecule while the signal wave receives the energy from the molecule. We treat these processes as an indirect energy transfer from the pumping to the signal.

We imply that all involved systems perform coherent oscillations. To determine the direction of the energy transfer between the electric dipole moment of a molecule and the incident wave, we study the phase difference between the driven oscillation of the dipole moment and the wave (see Remark 13.1).

In the stationary regime, the total energy of oscillations of the dipole moment of the molecule should not change, but there is an exchange of energies between the responses of the dipole moment at different wavelengths. On each frequency, the molecule may absorb or radiate energy. Since the interaction between electronic and vibronic subsystems of the molecule is weak, we consider the absorption-radiation process on each frequency separately.

Since, in this section, we are interested in the energy exchange between the responses on frequencies ω_P and ω_S, we only consider the terms $\left(S_{\omega_S}+S^{(g)}_{\omega_S}\right)e^{-i\omega_S t}$ and $\left(S_{\omega_P}+S^{(g)}_{\omega_P}\right)e^{-i\omega_P t}$ in Eq. (13.1.18). Studying the mechanism of this exchange, we assume, for a moment, that the intensity of the pumping and signal waves are constant and consider the interaction of the waves with the molecule separately.

We begin with considering the wave-molecule interaction on the frequency ω_S. Equation (13.1.18) is reduced to

$$d\widehat{\sigma}_3^{(g,\omega_S)}/dt+(i\omega_\sigma+\gamma_\sigma)\widehat{\sigma}_3^{(g,\omega_S)}\simeq\left(S_{\omega_S}+S^{(g)}_{\omega_S}\right)e^{-i\omega_S t}. \tag{13.1.25}$$

In a typical experimental situation, the amplitude of the pump wave is much larger than that of the Stokes wave $\Omega_P\gg\Omega_S$; therefore, the terms S_{ω_S} and $S^{(g)}_{\omega_S}$ can be simplified—in S_{ω_S} and $S^{(g)}_{\omega_S}$, we can retain the terms proportional to $|\Omega_P|^2\Omega_S$ only. Taking into account that $\omega_\sigma\gg\omega_S$, ω_P and $\omega_B=\omega_\nu$, we can reduce S_{ω_S} and $S^{(g)}_{\omega_S}$ from (13.1.19) and (13.1.20) to

$$S_{\omega_S}\simeq\frac{i|\Omega_P|^2\Omega_S}{2(\omega_S-\omega_\sigma)^2},\qquad S^{(g)}_{\omega_S}=\frac{ig^2|\Omega_P|^2\Omega_S}{8(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)^2(\omega_B-\omega_\nu-i\gamma_\nu)}. \tag{13.1.26}$$

Then, Eq. (13.1.25) takes the form:

$$d\widehat{\sigma}_3/dt+(i\omega_\sigma+\gamma_\sigma)\widehat{\sigma}_3=\left(\frac{g^2}{4(\omega_\sigma-\omega_P)^2(\omega_B-\omega_\nu-i\gamma_\nu)}+\frac{1}{\omega_\sigma-\omega_S}\right)\frac{i|\Omega_P|^2\Omega_S}{2(\omega_\sigma-\omega_S)}e^{-i\omega_S t}. \tag{13.1.27}$$

The steady-state solution to this equation is

$$\widehat{\sigma}_3=\left(\frac{1}{\omega_\sigma-\omega_S}+i\frac{g^2}{(\omega_\sigma-\omega_P)^2(\omega_B-\omega_\nu-i\gamma_\nu)}\right)\frac{|\Omega_P|^2\Omega_S e^{-i\omega_S t}}{2(\omega_\sigma-\omega_S)^2}\widehat{I}. \tag{13.1.28}$$

Note that at the exact resonance, $\omega_B=\omega_\nu$, expression (13.1.28) reduces to

$$\widehat{\sigma}_3 = \left(\frac{1}{\omega_\sigma - \omega_P} + i \frac{g^2}{4\gamma_v (\omega_\sigma - \omega_S)^2} \right) \frac{|\Omega_P|^2 \Omega_S e^{-i\omega_S t}}{2(\omega_\sigma - \omega_P)^2} \widehat{I}. \tag{13.1.29}$$

Remark 13.1 The Work Done by the External Field on the Dipole
Consider a linear dipole that performs forced oscillations:

$$\mathbf{d}(t) = \mathbf{d}_0 \cos(\omega t + \varphi) = \alpha \mathbf{E}_0 \cos(\omega t + \varphi)$$

under the action of an external field $\mathbf{E}(t) = \mathbf{E}_0 \cos \omega t$. Here φ is the phase difference, and α is the absolute value of the dipole polarizability. The work done by the external field on the dipole averaged over the period $T = 2\pi/\omega$ is [6]

$$\overline{W} = \overline{\int \mathbf{E} \cdot d\mathbf{d}} = \frac{1}{T} \int \mathbf{E}(t) \cdot \frac{d}{dt}(\mathbf{d}(t)) dt = -\frac{1}{T} \int_0^T \alpha E_0^2 \cos(\omega t) \sin(\omega t + \varphi) dt = -\frac{1}{2} \alpha \omega E_0^2 \sin \varphi.$$

When the phase belongs to the interval $(-\pi, 0)$, the field does a positive work on the oscillator. This means that energy is transferred from the external field to the oscillator. If $0 < \varphi < \pi$, then the work of the external field over the dipole is negative, which can be interpreted as the energy transfer from the dipole to the external field.

The first term on the right-hand side of Eq. (13.1.29) is related to the nonlinearity of the electronic subsystem modeled by a TLS. This term does not take into account oscillations of the nuclear subsystem. The phase of this term coincides with the phase of the external field with the frequency ω_S. Therefore, the nonlinearity of the electronic subsystem does not lead to the amplification of the signal beam. It is the second term that results in the phase shift between $\widehat{\sigma}_3$ and the external field $\Omega_S(\omega_S)$, which equals $\pi/2$.

Indeed, from the second term on the right-hand side of Eq. (13.1.29), we obtain the third-order correction to the dipole moment induced by the signal wave:

$$\begin{aligned} \mathbf{d}_3^{(g)}(\omega_S) &= d_{eg} \sigma_3^g(\omega_S) = d_{eg} i \frac{1}{8} \frac{g^2}{\gamma_v} \frac{|\Omega_P|^2 \Omega_S e^{-i\omega_S t}}{(\omega_\sigma - \omega_P)^2 (\omega_\sigma - \omega_S)^2} \\ &= \frac{d_{eg}^2 g^2 |\Omega_P|^2}{8\hbar\gamma_v (\omega_\sigma - \omega_P)^2 (\omega_\sigma - \omega_S)^2} \left(\frac{-\hbar\Omega_S}{d_{eg}} \right) \exp(-i(\omega_S t + \pi/2)) \\ &= \alpha_S E_S \exp(-i\pi/2) \exp(-i\omega_S t)/4, \end{aligned} \tag{13.1.30}$$

where

$$\alpha_S^{(3)} = \frac{d_{eg}^2 g^2 |\Omega_P|^2}{\hbar\gamma_v(\omega_\sigma - \omega_P)^2(\omega_\sigma - \omega_S)^2}$$

is the nonlinear polarizability at the frequency ω_S. The phase difference between oscillations of the dipole and the field at the frequency ω_S is $\pi/2 \in (0, \pi)$. Consequently, the work done by the field is negative, indicating that the energy flows from the dipole moment to the field. Below, we show that this results in the amplification of the field at the frequency ω_S while the wave propagates in the medium.

The energy transferred to the wave with the frequency ω_S is supplied by the wave with the frequency ω_P. To see this, let us consider the response of the molecule polarization at the frequency ω_P in the third order of the perturbation theory. For this purpose, on the right-hand side of Eq. (13.1.25), we leave only the terms that are proportional to $e^{-i\omega_P t}$. Also, since we consider the resonant case, $\omega_P - \omega_S = \omega_v$, we retain only the term $S_{\omega_P}^{(g)}$ to obtain

$$d\widehat{\sigma}_3/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_3 \simeq S_{\omega_P}^{(g)} e^{-i\omega_P t}. \tag{13.1.31}$$

Assuming that $\Omega_P \gg \Omega_S$, $\omega_\sigma \gg \omega_S$, ω_P, and $\omega_\sigma - \omega_S \sim \omega_\sigma - \omega_P$, the term $S_{\omega_P}^{(g)}$ can be simplified:

$$S_{\omega_P}^{(g)} = \frac{g^2}{8\gamma_v} \frac{|\Omega_S|^2 \Omega_P}{(\omega_\sigma - \omega_S)^2(\omega_\sigma - \omega_P)} \tag{13.1.32}$$

Using Eq. (13.1.32), we obtain the solution to Eq. (13.1.31) in the form:

$$\widehat{\sigma}_3(t) = -\frac{1}{8}\frac{g^2}{\gamma_v} \frac{|\Omega_S|^2 \Omega_P e^{-i(\omega_P t + \pi/2)}}{(\omega_\sigma - \omega_P)^2(\omega_\sigma - \omega_S)^2} \tag{13.1.33}$$

$$\begin{aligned}
\mathbf{d}_3^{(g)}(\omega_P) &= d_{eg}\sigma_3^g(\omega_P) = -d_{eg} i \frac{1}{8}\frac{g^2}{\gamma_v} \frac{|\Omega_S|^2 \Omega_P e^{-i\omega_P t}}{(\omega_\sigma - \omega_P)^2(\omega_\sigma - \omega_S)^2} \\
&= \frac{d_{eg}^2 g^2 |\Omega_S|^2}{8\hbar\gamma_v(\omega_\sigma - \omega_P)^2(\omega_\sigma - \omega_S)^2} \left(\frac{-\hbar\Omega_P}{d_{eg}}\right) \exp(-i(\omega_P t - \pi/2)) \\
&= \alpha_P E_P \exp(i\pi/2) \exp(-i\omega_P t)/4,
\end{aligned} \tag{13.1.34}$$

Comparing Eqs. (13.1.30) and (13.1.34), one can see that the phase shift between the pump and signal responses equals π. Thus, the pump wave performs a positive work on a Raman-active molecule, while the Stokes wave performs a negative work (see Remark 13.1). Hence, the pump wave through the molecule transfers energy to the Stokes wave.

As one can see from Eq. (13.1.29), the resonant responses of the molecular dipole moment $\widehat{\sigma}_3^{\omega_P}(t)$ on the frequencies ω_P and ω_S have the opposite signs. Thus, the

external field E_P drives the motion of the electronic subsystem at the frequency ω_P, performing positive work on the subsystem, while the field E_S performes negative work on the subsystem.

13.2.2 Raman Amplification in Terms of Nonlinear Optics

In the previous subsection, we have considered the amplification of the signal wave due to the energy transfer from the pump wave. The key moment in the energy transfer process is the phase shift. Thus, it is the coherent parts of the waves that take part in this process. The coherent parts of the fields are well-described by the classical Maxwell equations. Since the molecule is considered a quantum system, such a description is semiclassical. This approach is adequate for experiment conditions when incident fields are powerful coherent light beams (the number of photons is large). That is why the Raman amplification can also be described in terms of nonlinear optics. Indeed, if we consider the coherent component of the scattered light, we can see that the obtained expressions are similar to the description of the nonlinear mixing of two incident waves given by the third-order nonlinear susceptibility, which relates the third-order polarization to the electric field [3, 7]:

$$P^{(3)}(\omega_s, \omega_p) = \chi^{(3)}(\omega_s, \omega_p, \omega_s, -\omega_p) E(\omega_P) E(\omega_S) E^*(\omega_P). \tag{13.1.35}$$

where E is the Fourier transform of the electric field.

The consistent derivation of the expression for $\chi^{(3)}(\omega_s, \omega_p, \omega_s, -\omega_p)$ requires the quantum mechanical approach, while the scattering of waves on a molecule may be considered as a classical nonlinear process of mixing four plane waves. The expression for $\chi^{(3)}(\omega_S, \omega_P, \omega_S, -\omega_P)$ may also be obtained in a classical consideration of the nuclear motion by introducing a phenomenological Hamiltonian and applying a strong assumption that the system of nuclei can radiate at optical frequency [1]. Below, we obtain the expression for $\chi^{(3)}(\omega_S, \omega_P, \omega_S, -\omega_P)$ in the quantum mechanical approach.

The third-order polarization is related to $\langle \widehat{\sigma}_3 \rangle$ as $P^{(3)} = n d_{\mathrm{eg}} \langle \widehat{\sigma}_3 \rangle$. Then, using Eq. (13.1.29) we can determine the quantum expression for nonlinear susceptibility as

$$\chi^{(3)}(\omega_S, \omega_S, \omega_P, -\omega_P) = \frac{1}{2} \frac{n d_{\mathrm{eg}}^4}{\hbar^3} \frac{1}{(\omega_\sigma - \omega_S)(\omega_\sigma - \omega_P)^2} \times \left[1 + \frac{1}{4} \frac{g^2}{(\omega_P - \omega_S - \omega_{\mathrm{v}} - i\gamma_{\mathrm{v}})(\omega_\sigma - \omega_S)} \right] \tag{13.1.36}$$

This equation shows that the maximum nonlinear response occurs when the difference in the frequencies ω_S and ω_P is equal to the frequency of the nuclear vibrations ω_{v}.

Generally, $\chi^{(3)}(\omega_{out};\omega_{in1},\omega_{in2},\omega_{in3})$ characterizes a process in which three incident waves with different frequencies ω_{in1}, ω_{in2}, and ω_{in3} are mixed, resulting in one output wave with the frequency ω_{out}. In the case of the Raman amplification, we have $\omega_{in1} = \omega_P$, $\omega_{in2} = \omega_S$, $\omega_{in3} = -\omega_P$, and $\omega_{out} = \omega_S$. Thanks to energy conservation, there are four possible processes with output frequencies $2\omega_S - \omega_P$, ω_S, ω_P, and $2\omega_P - \omega_S$ (see Eqs. (13.1.22) and (13.1.23)) [8].

Now, as we have the nonlinear susceptibility, we can determine the change in the signal amplitude due to the scattering. For this, we need to find the electric fields $\mathbf{E}_P$ and $\mathbf{E}_S$.

The dynamics of the electric field $\mathbf{E}$ in a homogeneous medium is described by the wave equation, which can be obtained from Maxwell's equations:

$$\nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} = -\frac{1}{c^2}\frac{\partial^2 \mathbf{P}}{\partial t^2} \tag{13.1.37}$$

where $\mathbf{P}$ is the specific polarization of the medium and $\mathbf{E} = \mathbf{E}_P + \mathbf{E}_S$ is the total field. We represent the specific polarization as a sum $\mathbf{P} = \mathbf{P}_{\mathrm{L}} + \mathbf{P}^{(3)}$ of the linear part $\mathbf{P}_{\mathrm{L}}$, which is proportional to the amplitude of the incident field, and the nonlinear part $\mathbf{P}^{(3)}$ associated with both the saturation of the electronic levels of the molecule and the Raman processes, such as the parametric modulation of the oscillations of the electronic subsystem of molecules.

The linear part of the specific polarization of the medium $\mathbf{P}_{\mathrm{L}}$ is connected with the field $\mathbf{E}$ by the usual relation [6]:

$$\mathbf{P}_{\mathrm{L}} = (\varepsilon_d - 1)\mathbf{E}. \tag{13.1.38}$$

Here ε_d is a value of the linear permittivity. (Equation (13.1.38) is written in the time domain representation; therefore, generally, the permittivity ε_d is an operator.) Substituting Eq. (13.1.38) into Eq. (13.1.37), we obtain:

$$\nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2}\frac{\partial^2 (\varepsilon_d \mathbf{E})}{\partial t^2} = -\frac{1}{c^2}\frac{\partial^2 \mathbf{P}^{(3)}}{\partial t^2}. \tag{13.1.39}$$

We assume the total field may be represented as a sum of two traveling along the z-axis plane monochromatic waves $E_P(z,t)$ and $E_S(z,t)$ with frequencies ω_P and ω_S ($\omega_S < \omega_P$) and the same polarizations $\mathbf{e}_\mathbf{x}$. Practically, we disregard the frequency dispersion of the linear permittivity and consider it as a c-constant. This allows us to consider the evolution of the intensity of each wave:

$$\mathbf{E}(z,t) = E_P(z,t)\mathbf{e}_\mathbf{x} + E_S(z,t)\mathbf{e}_\mathbf{x} \tag{13.1.40}$$

with

$$E_P(z,t) = \frac{1}{2}\left(A_P(z)e^{i(k_P z - \omega_P t)} + A_P^*(z)e^{-i(k_P z - \omega_P t)}\right) \tag{13.1.41}$$

$$E_S(z,t) = \frac{1}{2}\left(A_S(z)e^{i(k_S z - \omega_S t)} + A_S^*(z)e^{-i(k_S z - \omega_S t)}\right) \tag{13.1.42}$$

Then,

$$\begin{aligned}\varepsilon_d \mathbf{E}(z,t) = &\frac{1}{2}\varepsilon_d(\omega_S)\left(A_S(z)e^{i(k_S z - \omega_S t)} + A_S^*(z)e^{-i(k_S z - \omega_S t)}\right)\mathbf{e_x} \\ &+\frac{1}{2}\varepsilon_d(\omega_P)\left(A_P(z)e^{i(k_P z - \omega_P t)} + A_P^*(z)e^{-i(k_P z - \omega_P t)}\right)\mathbf{e_x}\end{aligned} \tag{13.1.43}$$

Due to $\mathbf{P}^{(3)}$, this field causes the nonlinear polarization of the medium. Primarily, we are interested in the nonlinear response at the frequency ω_S:

$$\mathbf{P}^{(3)} = \chi^{(3)}(\omega_S;\omega_S,\omega_P,-\omega_P)\mathbf{e_x}A_S(z)A_P(z)A_P^*(z)e^{-i(k_S z - \omega_S t)} \tag{13.1.44}$$

where the susceptibility $\chi^{(3)}(\omega_S;\omega_S,\omega_P,-\omega_P)$ is determined by Eq. (13.1.36). The maximum nonlinear response is observed when Eq. (13.1.22) is satisfied.

To focus on the nonlinear coupling of the electron subsystems and the nuclear vibrations of molecules, we leave only the resonant term $\omega_P - \omega_S = \omega_\nu$ in Eq. (13.1.36). It should be noted that even in the resonance $g^2/\gamma_\nu(\omega_\sigma - \omega_S) = (g/\gamma_\nu)(g/(\omega_\sigma - \omega_S)) \sim (g/\gamma_\nu)\varepsilon$ because $(g/\gamma_\nu) \sim \omega_\nu/\gamma_\nu \sim Q_\nu > 1$; we consider molecules in which $(g/\gamma_\nu)\varepsilon > 1$ (see Eq. (13.1.6)). Finally, we arrive at the following expression:

$$\chi^{(3)}(\omega_S,\omega_S,\omega_P,-\omega_P) \approx i\frac{nd_{\mathrm{eg}}^4}{8\hbar^3}\frac{g^2}{\gamma_\nu}\frac{1}{(\omega_\sigma - \omega_S)^2(\omega_0 - \omega_P)^2} \tag{13.1.45}$$

Substituting Eq. (13.1.45) into Eq. (13.1.44), we have:

$$\mathbf{P}^{(3)} = i\left|\chi^{(3)}\right|A_S(z)|A_P(z)|^2 e^{i(k_S z - \omega_S t)}\mathbf{e_x} \tag{13.1.46}$$

From Eq. (13.1.46) one can see that the nonlinear coupling of the electronic subsystems and the nuclear vibrations of molecules results in the induction of a specific polarization of the medium, which phase leads the external field $E(\omega_S)$ by $\pi/2$. This means that the polarization of the media, induced by the field $E(\omega_P)$, transfers the energy to the field $E(\omega_S)$. In other words, under the influence of the field $E(\omega_P)$, the molecule radiates a part of its energy into the field $E(\omega_S)$. It can be treated as the energy transfer from the field $E(\omega_P)$ to the field $E(\omega_S)$. The latter can be shown by substituting Eq. (13.1.42) for the electric field into wave equation (13.1.39) and using the paraxial optics approximation $|k_S A_S(z)| \gg |\partial A_S(z)/\partial z|$. In this case, the left-hand side of Eq. (13.1.39) takes the form:

$$\begin{aligned}\nabla\times\nabla\times\mathbf{E}+\frac{1}{c^2}\frac{\partial^2\varepsilon\mathbf{E}}{\partial t^2}&=-\nabla\cdot\nabla\mathbf{E}+\frac{\varepsilon}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}\\&=-\frac{1}{2}\left[\left(\frac{\partial^2}{\partial z^2}A_S(z)+2ik_S\frac{\partial}{\partial z}A_S(z)-ik_S^2\mathrm{Im}\varepsilon(\omega_S)A_S(z)\right)e^{i(k_Sz-\omega_St)}\right]\mathbf{e}_\mathbf{x}+\mathrm{h.c.}\\&\approx\left[-ik_S\frac{\partial}{\partial z}A_S(z)-ik_S^2\mathrm{Im}\varepsilon(\omega_S)A_S(z)\right]e^{i(k_Sz-\omega_St)}\mathbf{e}_\mathbf{x}+\mathrm{h.c.}\end{aligned}\tag{13.1.47}$$

where we used that

$$k_S^2=\frac{\omega_S^2}{c^2}\,\mathrm{Re}\,\varepsilon(\omega_S)\tag{13.1.48}$$

Now, we substitute Eqs. (13.1.47) and (13.1.46) into wave equation (13.1.39) to obtain

$$\frac{\partial}{\partial z}A_S(z)=\left(\left|\chi^{(3)}\right||A_P(z)|^2-\mathrm{Im}\varepsilon(\omega_S)\right)k_SA_S(z)/2\,\mathrm{Re}\,\varepsilon(\omega_S)\tag{13.1.49}$$

In the same way, we can obtain an equation for $A_P(z)$:

$$\frac{\partial}{\partial z}A_P(z)=\left(-\left|\chi^{(3)}\right||A_P(z)|^2-\mathrm{Im}\varepsilon(\omega_P)\right)k_PA_P(z)/2\,\mathrm{Re}\,\varepsilon(\omega_P)\tag{13.1.50}$$

Equation (13.1.49) shows that, thanks to $|A_P(z)|^2$, the pump field contributes to an increase in the signal field $A_S(z)$, while the term $\sim(-|A_P(z)|^2)$ in Eq. (13.1.50) causes a decrease in the field $A_P(z)$. This can be interpreted as an energy transfer from the pump field to the signal field.

When

$$|A_P(z)|^2>\mathrm{Im}\varepsilon(\omega_S)/\left|\chi^{(3)}\right|\tag{13.1.51}$$

the pump power is sufficient for an increase of the signal field as it travels through the medium. Historically, this enhancement has been attributed to the SRS of the pump wave into the signal wave and is called the Raman amplification.

Figure 13.1 illustrates the energy transfer in the SRS process. At the initial point $z=0$, there is a large pump field and a small signal field. At small distances from the source, the energy transferred from the large pump field compensates for the loss of the signal field, characterized by $\gamma_s=k_S\mathrm{Im}\sqrt{\varepsilon(\omega_S)}$. As a result, the signal field increases as it propagates in the system. At large distances, the pump field weakens, and the energy transferred to the signal field is no longer sufficient to compensate for the signal loss (inequality (13.1.51) is no longer satisfied), so that both the signal and pump intensities fall off.

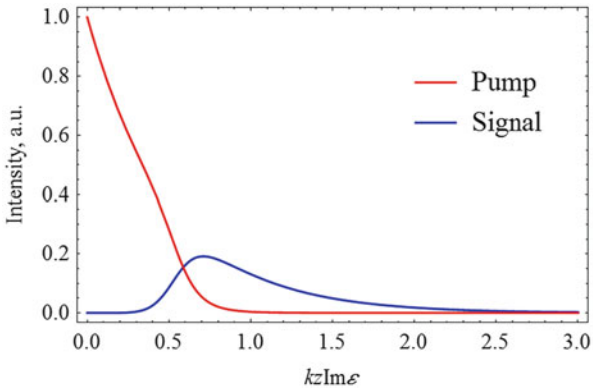

Fig. 13.1 The dependence of the pump (the red line) and the signal (the blue line) field intensities on the coordinate in SRS

To summarize, in this subsection, by employing Eq. (13.1.36) for the nonlinear susceptibility $\chi^{(3)}$, we show that while considering the coherent parts of Raman scattering, the Raman amplification may be described by classical fields.

13.3 The Phenomenon of "Stimulated Raman Scattering (SRS)"

SRS is observed in gases [9, 10], liquids [11, 12], and solids [13, 14]. The most important applications of the phenomenon are the visualization of biological samples [15] and signal amplification in telecommunication fibers [16].

Often, the quantum description of SRS, or rather of the Raman amplification, is based on a generalized description of the ordinary Raman effect [17] as a two-photon process that employs virtual levels (see Chap. 9, Fig. 9.3). In contrast to the spontaneous Raman scattering, in SRS, it is assumed that there are coherent photons at Stokes frequency, $\omega_S = \omega_P - \omega_v$, and the excited molecules at the virtual level. By absorbing a photon with the energy $\hbar\omega_P$ from the pump wave, the atom goes to the virtual level (left blue arrow in Fig. 9.3). Then, according to Einstein's theory (see Remark 13.2), emitting coherent photons with the energy $\hbar\omega_S$, the virtual state decays through a spontaneous and stimulated process, passing to the ground level with one excited vibron (green arrow in Fig. 9.3). This process leads to the amplification of the primary weak coherent Stokes wave. Thanks to this interpretation, this phenomenon is called stimulated Raman scattering.

Adding a resonator to the described scheme increases the life of the photon in the resonator. The decay of the next excited atom occurs in the presence of the earlier emitted photon. After each emission, the number of photons increases. That is, the cavity mode is amplified, which in turn leads to an increase in the probability of the decay process through stimulated emission. Thus, at a sufficiently high population of

the virtual level, a conventional generator scheme is implemented—an amplifier with positive feedback. This scheme describes the operation of a Raman laser, which is similar to the operation of a conventional laser.

Remark 13.2 Einstein Coefficients
Developing Bohr's idea, Einstein showed that the transition between high and low levels of an atom under the action of a monochromatic EM wave is due to the three processes—stimulated absorption, stimulated emission, and spontaneous emission. The probabilities of these processes are called *Einstein coefficients*.

The greater the intensity of traveling light, the higher the probability of the first two processes compared to the spontaneous emission. For us, it is important that at spontaneous emission, photons are emitted in any direction, while at stimulated absorption and stimulated emission, photons are absorbed from or radiated in the direction of the incident wave. The propagation of an intense incident wave is mainly determined by the first two processes.

For lasing, the stimulated emission should prevail over the spontaneous absorption. This implies the existence of the population inversion to enhance the wave. That is, the number N_U of atoms in the upper-level state should be greater than the number N_L of atoms in the lower-level state. The greater the difference $N_U - N_L$, the higher the amplification. The stimulated emission is the main mechanism for generating coherent light in amplified spontaneous emission (ASE) [18] and lasing.

The physical difference between Raman and conventional lasers is that the Raman amplification is caused not by the inverse population of the excited (virtual) level but by the transfer of energy from the pump wave to the cavity mode due to the nonlinear properties of the active medium. However, this requires the presence of a coherent part of the radiation at the Stokes frequency.

Another feature of Raman laser is that the amplification occurs due to coherent pumping, the frequency of which is related to the generation frequency ω_{gen} by the relation $\omega_{gen} = \omega_P - \omega_v = \omega_{St}$. Therefore, to maintain generation, a coherent pump wave generator is needed. This is usually another laser that is pumped by incoherent radiation.

The experimental configuration for observing Raman lasing is notably straightforward: it involves a resonator excited by a laser operating at the frequency ω_P. This resonator is filled with a medium comprised of Raman-active molecules, characterized by a vibrational frequency ω_v. For the sake of simplicity, we assume that the resonator has a singular resonant frequency $\omega_R = \omega_P - \omega_v = \omega_{St}$ with a finite linewidth.

In such a setting, a weak field at the Stokes frequency is generated within the resonator. The initial increase in the number of photons in the resonator mode occurs due to the Purcell effect, which increases the probability of radiation into the cavity

mode. Given the finite quality factor of the resonator, a part of photons at the Stokes frequency accumulate within the resonator mode. Other photons either dissipate or exit the resonator if the system is open.

At this stage, the field inside the resonator is still incoherent. The coherence arises due to the Bose statistics of photons. The probability of radiation into a specific mode with a given phase increases proportional to the number of photons already occupying that mode. The other photons are emitted into resonator modes with different phases; they form incoherent radiation. This differs from the process of stimulated emission predicted by Einstein, who assumed that photons are always emitted into the mode of incident radiation with a given phase. Instead, the photons are more likely to be emitted into the mode containing the highest number of photons. Initially, the preference for photons being emitted into this mode might be weak. Since the coherence of Raman scattering is determined by the coherence of vibrons, their presence is an additional and decisive factor in forming Raman lasing. Therefore, Raman amplification is a collective phenomenon but not a result of successive single events of stimulated emission.

At the resonator's output, we observe a signal whose intensity is determined by the Q-factor of the resonator, the efficiency of the signal output from the resonator, and the intensity of the incident pumping wave. Naturally, even with coherent pumping, the signal output is incoherent.

Initially, while the vibrational modes in the molecule are thermal, no additional phenomenon unfolds. Illumination of the resonator at the Stokes frequency does not yield any amplification. Therefore, we cannot talk about stimulated Raman amplification at this stage.

As the pumping amplitude increases, coherent vibrons and Stokes photons build up in the resonator. In essence, two coherent wave components emerge within the resonator, with a frequency difference equal to the Stokes shift. As we have seen, this scenario leads to the amplification of the Stokes wave through the pumping wave—a phenomenon commonly recognized as Raman amplification. In turn, the amplification of the coherent part of the Stokes wave increases the number of coherent photons (see Sect. 13.4 for details). This process can be referred to as stimulated Raman emission, albeit distinct from the conventional Einsteinian mechanism. Sooner or later, self-oscillations arise in the resonator, and these oscillations involve both photons and vibrons [19, 20].

The occurrence of Raman lasing oscillations depends on the interplay between the resonator's Q-factor and the vibron's quality factor. This could potentially lead to Raman instability within the molecule, in which coherent vibrons and the incoherent Stokes signal are amplified. In scenarios where the Q-factors are comparable, optical lasing occurs alongside the buildup of coherent vibrons. The operation of the laser in the regime of well-developed coherent vibrons is discussed in Chap. 14.

13.4 Coherent Anti-Stokes Raman Scattering (CARS)

In this section, we continue considering the coherent Raman phenomena caused by the illumination of a Raman-active molecule with two coherent waves.

As shown in Chap. 12, spontaneous Raman scattering and SERS give an incoherent Raman response. The reason for this is that only thermal vibrons take part in the Raman scattering process. An increase in the intensity of the incident beam and/or making it coherent does not result in a coherent Raman response. As shown in Sect. 13.1, in the case of two incident coherent waves (pump and signal), due to the nonlinearity of the Fröhlich interaction between the electronic and vibronic subsystems, a beat frequency (the difference between pump and signal frequencies) appears in the spectrum of the driving force in the equation for vibrons. If the beat frequency coincides with the eigenfrequency of nuclear oscillations, the resonant excitation of coherent vibrons begins, leading to the coherent Raman response.

The considered in Sect. 13.1 coherent Raman response is very weak compared to incoherent responses. The situation can be improved if we take into account a response from many molecules. In this case, the intensity of the incoherent signal is proportional to the number of molecules N, while the response of the coherent signal may be proportional to N^2. Thus, to increase the coherent radiation, we should synchronize the oscillations of the molecules. For this purpose, in the case of Raman laser, many molecules are placed in a high-Q resonator. Studying CARS, we consider N Raman-active molecules occupying a subwavelength volume. If the number of molecules is large, the coherent response may be greater than the incoherent response. Thus, the CARS enhancement is a collective effect arising due to a quadratic increase of the coherent signal with an increase in the number N of molecules while the incoherent signal increases linearly.

In experiments on CARS, molecules are illuminated with two waves with frequencies ω_1 and ω_2 (we assume that $\omega_2 > \omega_1$). The difference in these frequencies $\omega_B = \omega_2 - \omega_1$ (the beat frequency) is chosen to be close to the vibrational frequency ω_v of the nuclei in the molecule [21–23]. In both CARS and the Raman laser, coherent vibrons are excited. The main difference between the Raman laser and CARS is that different mechanisms cause coherent vibron excitations. In the Raman laser, this mechanism is related to the beginning of auto-oscillations of both the photons on the Stokes frequency and vibrons. In CARS, the Stokes wave is an external one. Consequently, the coherent vibrons are parametrically excited.

Unlike the cases considered in the previous sections, in CARS, the incident beams are assumed to be so strong that because of the weakness of the Raman scattering, the energy transfer from one beam to the other can be neglected.

In spontaneous Raman scattering, the illumination of the molecule by a single monochromatic wave leads to responses at three different frequencies (Rayleigh, Stokes, and anti-Stokes). If we illuminate the molecule by two waves with frequencies ω_1 and ω_2, we could expect the responses on six frequencies—two Rayleigh frequencies ω_1 and ω_2, two Stokes frequencies $\omega_1 - \omega_v$ and $\omega_2 - \omega_v$, and two anti-Stokes frequencies $\omega_1 + \omega_v$ and $\omega_2 + \omega_v$. However, in the case of the resonance

$\omega_B = \omega_v$, instead of spontaneous Raman scattering, one observes more intensive CARS that is characterized by significant coherent responses on four frequencies only, namely, on two Rayleigh frequencies ω_1 and ω_2, the CSRS frequency, $\omega_{CSRS} = 2\omega_1 - \omega_2 = \omega_1 - \omega_v$, and CARS frequency $\omega_{CARS} = 2\omega_2 - \omega_1 = \omega_2 + \omega_v$.

The smallness of the involved Rabi frequencies compared to ω_1 and ω_2 allows us to employ the perturbation theory developed in Sect. 13.1 to perform quantitative estimations.

13.4.1 The Quantum Theory of the CARS

To describe the CARS effect, we use Hamiltonian (13.1.1). Since, in this section, we are interested in the anti-Stokes signal with the frequency $2\omega_P - \omega_S \equiv 2\omega_2 - \omega_1 = \omega_2 + \omega_B = \omega_{CARS}$, we only retain the terms proportional to $\exp(-i(2\omega_2 - \omega_1)t)$ in the right-hand side of Eq. (13.1.18). In contrast to the consideration of SRS, we should now take into account that $\Omega_P \sim \Omega_S$. As a result, disregarding the off-resonant terms, Eq. (13.1.18) is reduced to

$$d\widehat{\sigma}_3/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_3 = \left(S_{\omega_{caSt1}} + S^{(g)}_{\omega_{caSt}}\right)e^{-i\omega_{CARS}t} = iS_1S_2\Omega_2\left[1 - \frac{g^2}{2(\omega_B - \omega_v + i\gamma_v)(\omega_\sigma - \omega_2)}\right]e^{-i\omega_{CARS}t}. \tag{13.2.1}$$

Here, we use Eqs. (13.1.19) and (13.1.20) and introduce the notations:

$$S_1 = \frac{\Omega_1^*}{2(\omega_\sigma - \omega_1)}, \qquad S_2 = \frac{\Omega_2}{2(\omega_\sigma - \omega_2)} \tag{13.2.2}$$

The natures of the two terms in the square brackets on the right-hand side of Eq. (13.2.1) are different. The unity appears due to the natural nonlinearity of the molecule caused by the population saturation of the quantum levels of the electronic system; this term has no resonances and is usually considered as an off-resonant background. The second term relates to the interaction of the electronic and vibrational degrees of freedom of the molecule. Due to this interaction, the effect of the external field on the electronic subsystem leads to the excitation of coherent vibrons at the beat frequency ω_B. This phenomenon has a resonant nature; the resonance occurs at $\omega_B = \omega_v$. The presence of the second term means that the more vibrons we have, the more photons we obtain.

The dimensionless parameter that determines the ratio between the off-resonant background and the resonant signal of CARS is $g^2/\gamma_v|\omega_2 - \omega_\sigma|$ (see Eq. (13.2.1)). (This parameter is greater than unity if nuclear vibrations have a high-quality factor $Q_v = \omega_v/\gamma_v \sim g/\gamma_v \gg \omega_v/g$; see Eq. (13.1.5).). If $g^2/\gamma_v|\omega_2 - \omega_\sigma| > 1$, the CARS signal

significantly exceeds the background determined by the nonlinearity that does not depend on the Fröhlich interaction. For example, for molecules of acetonite and various oils, the magnitude $g^2/\gamma_v|\omega_2 - \omega_\sigma| \sim 10$ and the effect of CARS are strongly manifested; this is not so for polystyrene in which $g^2/\gamma_v|\omega_2 - \omega_\sigma| \sim 0.1$.

The solution to Eq. (13.2.1) is

$$\widehat{\sigma}_3 = \frac{\Omega_1\Omega_2^2}{4(\omega_\sigma - \omega_1)(\omega_\sigma - \omega_2)(\omega_\sigma - \omega_{CARS})}\left[1 - \frac{g^2}{2(\omega_B - \omega_v + i\gamma_v)(\omega_\sigma - \omega_2)}\right]e^{-i(2\omega_2 - \omega_1)t} \tag{13.2.3}$$

For a single molecule, the coherent response is much weaker than the incoherent one; it is however; increasing the number of molecules may reverse the relationship between signal amplitudes.

Note that that the response of $\widehat{\sigma}_3$ at the frequency $2\omega_2 - \omega_1$ (see Eqs. (13.1.17) and (13.2.2)) depends on

$$\widehat{b}_2 = \frac{g}{\omega_B - \omega_v + i\gamma_v}S_1S_2e^{-i(\omega_2 - \omega_1)t}. \tag{13.2.4}$$

Solution (13.2.4) corresponds to excitation of coherent vibrons when two incident monochromatic fields have the frequencies ω_1 and ω_2. Under the resonant excitation $\omega_B = \omega_v$, the number of coherent vibrons is equal to

$$n_b^{\text{coh}} = |b_2|^2 \approx \frac{1}{16}\left(\frac{\Omega_1}{\omega_1 - \omega_\sigma}\right)^2\left(\frac{\Omega_2}{\omega_2 - \omega_\sigma}\right)^2\left(\frac{g}{\gamma_v}\right)^2 \tag{13.2.5}$$

while the number of incoherent vibrons, according to Eq. (11.1.27), is

$$n_b^{\text{non-coh}} = \overline{n}_v = \frac{1}{\exp(\hbar\omega_v/kT) - 1} \tag{13.2.6}$$

Using the characteristic values $\omega_v \approx 100$ meV, $\gamma_v \approx 1$ meV, $g \approx 10$ meV, $\omega_\sigma \approx 3$ eV, $\Omega_1 \approx \Omega_2 \approx 10$ meV, and $T = 20$ meV [24–27] in Eqs. (13.2.5) and (13.2.6) gives $n_b^{coh}/n_b^{non-coh} \sim 10^{-7}$. In other words, the number of coherent vibrons is smaller by many orders of magnitude than the number of incoherent vibrons. However, the coherent response is proportional to the squared number of molecules N^2, while the spontaneous signal is proportional to N. Thus, the above estimates give that for $N \gg n_b^{\text{non-coh}}/n_b^{\text{coh}} \sim 10^7$, the coherent signal becomes larger than the incoherent one.

In CARS, the resonance condition is $\omega_B = \omega_v$; therefore, by varying ω_B in experiment, one can determine both ω_v and γ_v.

Let us consider how the change in the frequency ω_1 affects the spectrum of light scattering on a molecule. In the molecule, the electronic subsystem and the vibrational subsystem of nuclei couple, but only the electronic subsystem radiates. Therefore, the expression for the dipole moment of the electronic subsystem

$\widehat{\mathbf{d}}(t) = \mathbf{d}_{eg}\widehat{\sigma}(t)$ allows us to determine the spectrum of a signal scattered by the molecule. As we discuss in Chap. 11, the spectrum can be expressed as

$$I_{CARS}(\omega) \sim \left|\mathbf{d}_{eg}\right|^2 \mathrm{Re} \int_0^{+\infty} \left\langle \widehat{\sigma}_3^{\dagger}(t+\tau)\widehat{\sigma}_3(t) \right\rangle e^{-i\omega\tau} d\tau \tag{13.2.7}$$

Substituting expression (13.2.3) into Eq. (13.2.7), we obtain:

$$I_{CARS} \sim I(\omega)\delta(\omega_B + \omega_2 - \omega) = I(\omega)\delta(\omega_{CARS} - \omega) \tag{13.2.8}$$

where

$$I(\omega) \sim \left|\mathbf{d}_{eg}\right|^2 |S_1|^2 |S_2|^4 \left[1 + \frac{1}{4} \frac{g^4}{\left((\omega_B - \omega_v)^2 + \gamma_v^2\right)(\omega_2 - \omega_\sigma)^2}\right]. \tag{13.2.9}$$

Thus, as shown in Fig. 13.2, the maximum of the CARS signal is achieved at the vibron resonance.

Due to the interference of the nonresonant coherent background and the resonant coherent signal, the CARS and CSRS intensity profiles are asymmetrical.

If in Eq. (13.1.25) we consider the terms $S_{2\omega_S - \omega_P}$ and $S^{(g)}_{2\omega_S - \omega_P}$ oscillating with the frequency $2\omega_S - \omega_P = \omega_S - \omega_B = \omega_S - \omega_v = \omega_{CSRS}$, we obtain the intensity of the CSRS:

$$I_{CSRS} \sim \left|\mathbf{d}_{eg}\right|^2 |S_1|^4 |S_2|^2 \left[1 + \frac{1}{4} \frac{g^4}{\left((\omega_2 - \omega_1 - \omega_v)^2 + \gamma_v^2\right)(\omega_1 - \omega_\sigma)^2}\right] \delta(\omega_{CSRS} - \omega) \tag{13.2.10}$$

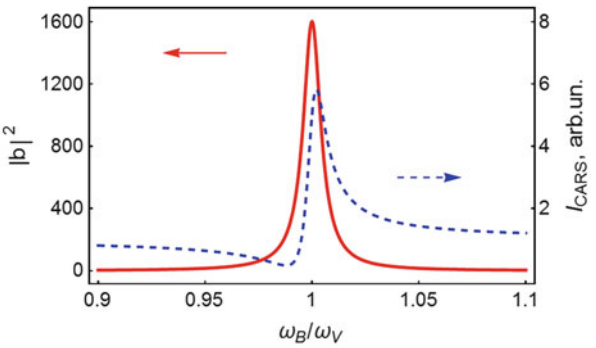

Fig. 13.2 The dependence of the square of the vibration amplitude (the red solid line) and intensity of CARS signal (the blue dashed line) on the beat frequency $\omega_B = \omega_2 - \omega_1$. The parameters of the system are $\omega_\sigma = 3\,\mathrm{eV}$, $\omega_2 = 2\,\mathrm{eV}$, $\omega_v = 100\,\mathrm{meV}$, $\gamma_v = 0.5\,\mathrm{meV}$, $g = 50$ meV

13.4.2 The Susceptibility of Third Order

As shown in the previous subsection, quantum mechanics predicts that if $\omega_2 - \omega_1 = \omega_v$, the vibrations of nuclei are resonantly excited by two coherent waves (see Eq. (13.2.4)). The arising vibrons are coherent. Consequently, the oscillations of the electronic subsystem are modulated by coherent vibrons, and the response of the electronic subsystem is also coherent.

Since the scattered signal is coherent, it can be considered as a classical field. From this point of view, CARS is a nonlinear four-wave mixing effect. That allows us to explain CARS employing the phenomenological theory of nonlinear optics [28, 29].

The key moment of the approach is the use of the nonlinear susceptibility of the third-order $\chi^{(3)}$. The expression for $\chi^{(3)}$ is usually obtained by the phenomenological approach, as described in Sect. 13.2.1 (see Eq. (13.1.35)). For CARS and CSRS, $\chi^{(3)}$ connects different waves, and we have to consider two susceptibilities:

$$P^{(3)}_{CARS}(\omega_1, \omega_2, \omega_{CARS}) = \chi^{(3)}(\omega_1, \omega_2, \omega_{CARS}) E(\omega_1) E^2(\omega_2) \tag{13.2.11}$$

and

$$P^{(3)}_{CSRS}(\omega_1, \omega_2, \omega_{CARS}) = \chi^{(3)}(\omega_1, \omega_2, \omega_{CSRS}) E^2(\omega_1) E(\omega_2). \tag{13.2.12}$$

Using the same algebra as for Eq. (13.1.36), we arrive at the following expressions for $P(t) = nd_{eg}\langle\widehat{\sigma}(t)\rangle$ [30–32]:

$$P^{(3)}_{CSRS} = \frac{1}{4} \frac{nd_{eg}\Omega_1^2\Omega_2}{(\omega_\sigma - \omega_{CSRS})(\omega_\sigma - \omega_1)(\omega_\sigma - \omega_2)} \left[1 + \frac{1}{2} \frac{g^2}{(\omega_B - \omega_v - i\gamma_v)(\omega_\sigma - \omega_1)}\right] e^{-i(2\omega_1 - \omega_2)t} \tag{13.2.13}$$

and

$$P^{(3)}_{CARS} = \frac{1}{4} \frac{nd_{eg}\Omega_1\Omega_2^2}{(\omega_\sigma - \omega_{CARS})(\omega_\sigma - \omega_1)(\omega_\sigma - \omega_2)} \left[1 + \frac{1}{2} \frac{g^2}{(\omega_B - \omega_v + i\gamma_v)(\omega_\sigma - \omega_2)}\right] e^{-i(2\omega_2 - \omega_1)t}. \tag{13.2.14}$$

where n is the concentration of molecules.

The susceptibility of the third order for CARS is

$$\chi^{(3)}_{CARS} = \frac{P^{(3)}_{CARS}}{E_1 E_2^2} = \chi^{(3)}_{CARS,OR} + \chi^{(3)}_{CARS,R} \tag{13.2.15}$$

It consists of two contributions: the off-resonant $\chi^{(3)}_{OR}$

$$\chi^{(3)}_{CARS,OR} = -n\frac{1}{4}\frac{d^4_{eg}}{(2\omega_2-\omega_1-\omega_\sigma)(\omega_1-\omega_\sigma)(\omega_2-\omega_\sigma)}\frac{1}{\hbar^3} \tag{13.2.16}$$

and the resonant $\chi^{(3)}_R$

$$\chi^{(3)}_{CARS,R} = n\frac{1}{8}\frac{d^4_{\mathrm{eg}}}{(2\omega_2-\omega_1-\omega_\sigma)(\omega_1-\omega_\sigma)(\omega_2-\omega_\sigma)}\frac{1}{\hbar^3}\frac{g^2}{(\omega_2-\omega_1-\omega_v+i\gamma_v)(\omega_2-\omega_\sigma)} \tag{13.2.17}$$

where we use the definition of the Rabi frequency $\Omega_{1,\,2} = d_{\mathrm{eg}}E_{1,\,2}/\hbar$. As one can see from Eq. (13.2.17), the resonant contribution $\chi^{(3)}_R$ associated with the interaction of the electronic subsystem with vibrons has a resonance at $\omega_2 - \omega_1 = \omega_v$; the width of this resonance is determined by the dissipation rate of vibrons γ_v. The off-resonance contribution arises due to the nonlinearity of the molecule response to an external field due to a finite number of levels (in this example, there are only two).

13.4.3 The Theory of CARS in Nonlinear Optics

Using the nonlinear susceptibility for the CARS configuration, we can describe the propagation of an additional external wave at the frequency $\omega_{CARS} = 2\omega_2 - \omega_1$. The wave equation has the form:

$$\nabla\times\nabla\times\mathbf{E}_{CARS} + \frac{1}{c^2}\frac{\partial^2\varepsilon_d\mathbf{E}_{CARS}}{\partial t^2} = -\frac{1}{c^2}\frac{\partial^2\mathbf{P}^{(3)}_{CARS}}{\partial t^2}. \tag{13.2.18}$$

Let us consider the wave with the polarization vector directed along the x-axis and propagating along the z-axis so that the wave can be presented as

$$\mathbf{E}_{CARS} = A_{CARS}(z)\mathbf{e}_x\exp(-i(\omega_{CARS}t - k_{CARS}z)).$$

Using the paraxial optics approximation $|k_{CARS}A_{CARS}(z)| \gg |\partial A_{CARS}(z)/\partial z|$, and the expression for the nonlinear polarization, $\mathbf{P}^{(3)}_{CARS} = \chi^{(3)}_{CARS}A^*_1A_2A_2\mathbf{e}_x e^{-i(\omega_{CARS}t - k_{CARS}t)}$, we obtain:

$$\begin{aligned}\nabla\times\nabla\times\mathbf{E}+\frac{1}{c^2}\frac{\partial^2\varepsilon\mathbf{E}}{\partial t^2} &= -\nabla\cdot\nabla\mathbf{E}+\frac{\varepsilon}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}\\ &= -\left(\frac{\partial^2}{\partial z^2}A_{CARS}(z)+2ik_{CARS}\frac{\partial}{\partial z}A_{CARS}(z)\right.\\ &\quad\left.-ik_{CARS}^2\mathrm{Im}\varepsilon(\omega_{CARS})A_{CARS}(z)\right)e^{i(k_{CARS}z-\omega_{CARS}t)}\mathbf{e_x}\\ &\approx\left(-2ik_{CARS}\frac{\partial}{\partial z}A_{CARS}(z)+ik_{CARS}^2\mathrm{Im}\varepsilon(\omega_{CARS})A_{CARS}(z)\right)e^{i(k_{CARS}z-\omega_{CARS}t)}\mathbf{e_x}\\ &= -\frac{1}{c^2}\frac{\partial^2\mathbf{P}_3^{\mathrm{aSt}}}{\partial t^2}=-\frac{\omega_{CARS}^2}{c^2}\chi_{CARS}^{(3)}E_1^*E_2^2e^{i(k_{CARS}z-\omega_{CARS}t)}\mathbf{e}_x\end{aligned} \tag{13.2.19}$$

where we use

$$k_{CARS}^2=\frac{\omega_{CARS}^2}{c^2}\,\mathrm{Re}\,\varepsilon(\omega_{CARS}) \tag{13.2.20}$$

From Eq. (13.2.19) we obtain the equation for $A_{CARS}(z)$:

$$\frac{\partial}{\partial z}A_{CARS}(z)+\frac{k_{CARS}}{2}|\mathrm{Im}\varepsilon(\omega_{CARS})|A_{CARS}(z)=-i\frac{\omega_{CARS}^2}{c^2}\chi^{(3)}(\omega_1,\omega_2,\omega_{CARS})A_1^*A_2^2 \tag{13.2.21}$$

which has the solution

$$A_{CARS}(z)=\left(A_{CARS}(z_0)+2i\chi^{(3)}A_1^*A_2^2\right)\exp\left(-\frac{k_{CARS}}{2}|\mathrm{Im}\varepsilon(\omega_{CARS})|z\right)-2i\chi^{(3)}(\omega_1,\omega_2,\omega_{CARS})A_1^*A_2^2 \tag{13.2.22}$$

At large $z\gg(k_{CARS}|\mathrm{Im}\varepsilon(\omega_{CARS})|)^{-1}$, this solution does not depend on z:

$$A_{CARS}(z)\simeq-2i\chi^{(3)}(\omega_1,\omega_2,\omega_{CARS})A_1^*A_2^2 \tag{13.2.23}$$

where $\chi^{(3)}(\omega_1,\omega_2,\omega_{CARS})$ has a maximum at $\omega_2-\omega_1=\omega_v$.

As discussed in the previous subsection, even though the number of coherent vibrons is smaller by many orders of magnitude than noncoherent vibrations, the CARS signal can dominate spontaneous Raman scattering in experiment. There are several reasons for this:

1. The CARS signal grows quadratically with the increasing concentration of molecules, while spontaneous Raman scattering grows linearly.
2. If the illuminated volume occupied by Raman-active molecules is anisotropic, then the coherent Raman signal is strongly directional (see Eq. (13.2.23)).

3. The width of the CARS signal spectrum is determined by the linewidth of the light sources and may be narrower than the width of the spontaneous Raman signal, which is determined by γ_v.

To summarize, it is the coherence that leads to a relatively strong signal in CARS. Due to the smallness of $\chi^{(3)}$, the average number of coherent vibrons responsible for CARS is $10^5 - 10^7$ times less than the number of thermal vibrons responsible for spontaneous Raman scattering. However, the spontaneous emission of Raman scattering is proportional to the number of molecules N in the spot of the flare, while the signals of the CARS and CSRS are proportional to N^2. Despite the smallness of $\chi^{(3)}$, the factor of N may make the latter signals much stronger than that of spontaneous Raman scattering.

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Chapter 14
Raman Effect in Non-Raman Lasers

In this chapter, we discuss the influence of nuclear vibrations in active materials with strong electron-phonon coupling on the amplifying properties of conventional lasers. Such materials as colloidal [1, 2] and epitaxial quantum dots (QDs) [3–5], perovskites [6–8], and dye molecules [9, 10] are characterized by a high gain and are widely used for miniaturizing lasers [11–13].

As a rule, observed conventional gain in such lasers is much greater than that due to the SRS. Therefore, even in lasers using active media with a strong electron-phonon interaction, the influence of optical phonons on laser operation is usually not exhibited. Nevertheless, such materials can have large Raman cross sections [14–17] that may lead to unusual laser behavior [18]. In addition, in such lasers, the action of the EM field on the electronic subsystem makes it possible to amplify phonons. Thus, in addition to a large light amplification, systems with a strong electron-phonon coupling may effectively amplify optical phonons and lead to the creation of phonon nanolasers [19].

In the amplifying media based on materials with a large Raman scattering cross section, the Fröhlich constant g may be comparable to or even larger than the Rabi constant responsible for coupling the resonator electric field and the active medium polarization [20, 21]. To be specific, we consider amplifying media based on QD (see Ref. [18] and Remark 14.1). However, the results of this subsection are applicable to other materials with strong electron-phonon coupling.

Remark 14.1 **Quantum Dots**

QDs are semiconductor nanocrystals with sizes ranging from 2 to 20 nm. Their small size gives them unique optical and electronic properties; for example, the emission wavelength of a QD depends on its size. The behavior of QDs arises from the confinement of charge carriers (electrons and holes) within a small volume. This confinement restricts the motion of charge

(continued)

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Remark 14.1 (continued)
carriers, resulting in quantized energy levels similar to the energy levels of atoms.

Usually, QDs have a transition frequency between their ground state and the first excited state in optical or IR ranges. Due to high anharmonism, transitions to higher energy levels are less probable under illumination by monochromatic light; therefore, these transitions do not significantly impact the QD behavior. For this reason, TLS is a good model for describing QDs.

QDs have a wide range of applications. These include displays, lasers, light-emitting diodes, bioimaging, solar cells, and quantum computing.

We model the operation of a laser consisting of a single-mode resonator with the frequency ω_a and QDs serving as an active medium. In QDs, excitations of the electronic degrees of freedom usually appear as excitons—quasiparticles formed by binding an electron and a hole. Excitons may interact with the quantized vibrations of QD nuclei—optical phonons (see Remark 2.1).

We consider a single optical phonon mode with the eigenfrequency ω_v. Since underlying lasing is a resonant phenomenon, the electronic subsystem of the QD can be modeled by a TLS, the ground state $|g\rangle$ of which is in the valence band, and the excited state $|e\rangle$ is in the conduction band; the transition frequency between these states is ω_σ.

We emphasize that we consider a conventional laser scheme that differs from the Raman laser that is discussed in Sect. 13.3. In this chapter, we study a laser whose resonator size L is small enough to ensure inequality $\Delta\omega \gg \omega_v$. Here $\Delta\omega \sim c/L$ is the difference between neighboring resonant frequencies. Thus, the effect of the Raman laser can be neglected. We assume that $L \ll c/\omega_v \sim 100\,\mu$m.

Our system can be described by

$$\widehat{H} = \hbar\omega_a \widehat{a}^\dagger \widehat{a} + \hbar\omega_\sigma \widehat{\sigma}^\dagger \widehat{\sigma} + \hbar\Omega_R \left(\widehat{a}\widehat{\sigma}^\dagger + \widehat{a}^\dagger \widehat{\sigma}\right) + \hbar\omega_v \widehat{b}^\dagger \widehat{b} + \hbar g \widehat{\sigma}^\dagger \widehat{\sigma}\left(\widehat{b}^\dagger + \widehat{b}\right). \tag{14.1.1}$$

In this Hamiltonian, unlike Hamiltonian (10.1.23), the TLS interacts with the quantized mode of the resonator rather than with the classical field of EM wave.

The Fröhlich constant can be evaluated by using the value of the Raman scattering cross section $\sigma_{Cross_section}$ at the Stokes frequency (Eq. (11.1.49)). The experimentally measured value of $\sigma_{Cross_section}$ for CdSe QDs is $\sigma_{Cross_section} \approx 4 \cdot 10^{-6}$ Å^2 [22]. Using the values of the phonon frequency $\omega_v \approx 0.025$ eV (such a frequency corresponds to the optical phonon in CdSe [23]) and the QD dipole moment $d_{eg} \approx 5 \div 10$ D, we obtain that the Fröhlich constant is of the order of $g \simeq 10^{-2}$ eV which we use in this chapter.

To describe relaxation processes, it is necessary to introduce reservoirs, which interact with electronic and phonon subsystems of the QD and the resonator mode.

We consider different reservoirs describing Ohmic losses in the resonator, energy relaxation of the exciton, energy relaxation of optical phonons, and the phonon reservoir responsible for exciton dephasing. Using the approach developed in Sects. 13.2.1 and 13.2.2, we arrive at the following equations of motion, which are the expanded Maxwell-Bloch equations for expectation values of the operators $\widehat{a}$, $\widehat{\sigma}$, $\widehat{b}$, and $\widehat{D}$ [14, 21, 24, 25]:

$$da/dt = (-i\omega_a - \gamma_a/2)a - i\Omega_R\sigma, \tag{14.1.2}$$

$$d\sigma/dt = (-i(\omega_\sigma + g(b + b^*)) - \gamma_\sigma/2)\sigma + i\Omega_R aD, \tag{14.1.3}$$

$$db/dt = (-i\omega_v - \gamma_v/2)b - ig(D + 1)/2, \tag{14.1.4}$$

$$dD/dt = -\left(\gamma_p + \gamma_D\right)(D - D_0) + 2i\Omega_R\left(a^\dagger\sigma - \sigma^\dagger a\right), \tag{14.1.5}$$

Solving Eqs. (14.1.2)–(14.1.5) does not allow for a detailed description of the spontaneous emission process but describes the stimulated emission rather well [21, 26]. These equations describe an indirect coupling between the resonator mode described by the operator $\widehat{a}$ and an optical phonon of the active medium described by the operator $\widehat{b}$. Indeed, Eq. (14.1.2) includes the interaction of the resonator mode with the TLS through the term $-i\Omega_R\sigma$, while Eq. (14.1.3) has the term $-ig(b + b^*)\sigma$ that couples the TLS with phonons. The direct interaction of the resonator mode with phonons is absent because we assume that QDs are Raman-active.

Below, we describe the various operational regimes of a laser by three parameters of the problem. The first parameter is the Fröhlich interaction constant g. At $g = 0$, we deal with conventional lasers. The second relevant parameter is the pump rate γ_p, which determines the transition to the lasing regime. Instead of γ_p, we describe the pump rate with the related parameter $D_0 = (\gamma_p - \gamma_D)/(\gamma_p + \gamma_D)$. The third parameter of our problem is the resonator eigenfrequency ω_a. Note that ω_σ is kept constant. This means that throughout this chapter, we deal with the resonant Raman effect.

14.1 The Semiclassical Theory of Conventional Laser

The conventional laser model includes a resonator whose eigenmode frequency is ω_R. The resonator is filled with atoms, for simplicity, modeled by a TLS with a transition frequency ω_σ and with a dipole moment described by the operator $\widehat{\sigma}$. To achieve lasing we should have $\omega_R \sim \omega_\sigma \sim \omega$, where ω is the frequency on which stimulated emission occurs. Assuming that all operators vary with frequency ω, passing to slowly varying operator amplitudes, and using the rotating wave approximation, the dipole interaction of the stimulated emission field with the TLS may be described by the model Hamiltonian, which includes the Hamiltonians of quantized resonator mode $\hbar\omega_R\widehat{a}_R^\dagger\widehat{a}_R$, TLS $\hbar\omega_\sigma\widehat{\sigma}^+\widehat{\sigma}$, and the dipole interaction of the mode with the atom (the Jaynes-Cummings Hamiltonian):

$$\widehat{H} = \hbar\omega_R \widehat{a}_R^{\dagger}\widehat{a}_R + \hbar\omega_\sigma \widehat{\sigma}^{\dagger}\widehat{\sigma} + \hbar\Omega_R\left(\widehat{a}_R^{\dagger}\widehat{\sigma} + \widehat{\sigma}^{+}\widehat{a}_R\right) \tag{14.1.6}$$

Now, we can obtain the Heisenberg equations of motions for operators $\widehat{a}_R$, $\widehat{\sigma}$, and the TLS population inversion $\widehat{D} = \widehat{\sigma}^{\dagger}\widehat{\sigma} - \widehat{\sigma}\widehat{\sigma}^{\dagger}$. Describing the relaxation of the TLS polarization due to spontaneous emission by the relaxation time τ_σ and the relaxation of the TLS population inversion to the constant unsaturated TLS population inversion D_0 by τ_D, we arrive at the Heisenberg-Langevin equations. The value of D_0 is maintained by external pumping. (See Problem 1.1.)

It is worth emphasizing that the spontaneous emission is described by the relaxation term and noises, while the stimulated emission is described by the Jaynes-Cummings Hamiltonian. Now, we can transition to slowly varying amplitudes $\widehat{a}_R, \widehat{\sigma} \sim \exp(-i\omega t)$. Note that the frequency ω is the frequency of self-oscillations that differs from both ω_R and ω_σ. It must be determined during the solution process.

For estimations, it is convenient to transition to observables of the operators $a_{pl} = \langle \widehat{a}_{pl} \rangle$, $\sigma = \langle \widehat{\sigma} \rangle$, and $D = \left\langle 2\widehat{\sigma}^{\dagger}\widehat{\sigma} - 1 \right\rangle$. The next approximation that is usually made is to assume that $\langle Da_R \rangle = \langle D \rangle \langle a_R \rangle$ [20, 25]. As a result, we arrive at the Maxwell-Bloch equations:

$$\frac{da_R}{dt} = (i\Delta - 1/\tau_a)a_R - i\Omega_R\sigma \tag{14.1.7}$$

$$\frac{d\sigma}{dt} = (i\delta - 1/\tau_\sigma)\sigma + i\omega_R a_R D \tag{14.1.8}$$

$$\frac{dD}{dt} = 2i\Omega_R\left(a_R^{*}\sigma - \sigma^{*}a_R\right) - \frac{1}{\tau_D}(D - D_0), \tag{14.1.9}$$

where $\delta = \omega - \omega_\sigma$ and $\Delta = \omega - \omega_R$.

Equations (14.1.7)–(14.1.9) have a trivial stationary solution $a = 0$, $\sigma = 0$, and $D = D_0$. At $D < D_{th}$ (where D_{th} is some value that should be found), this solution is stable, but it becomes unstable at $D > D_{th}$, when a new stable stationary solution arises.

To find the frequency ω, we need to use the stationary solution of Eqs. (14.1.7)–(14.1.9) at $D > D_{th}$. Eliminating σ, we arrive at the following equation in complex numbers to determine ω:

$$\left[\frac{1}{\Omega_R}(\delta - i/\tau_\sigma)(\Delta - i/\tau_a) + \Omega_R D\right] a = 0. \tag{14.1.10}$$

The real and imaginary parts of this equality give:

$$\tau_\sigma\delta = -\tau_a\Delta \tag{14.1.11}$$

$$D_{st} = D_{th} = \frac{1 + \Delta^2 (\tau_a)^2}{\Omega_R^2 \tau_a \tau_\sigma} \tag{14.1.12}$$

From Eq. (14.1.11), we obtain:

$$\omega = \frac{\omega_R \tau_a + \omega_\sigma \tau_\sigma}{\tau_a + \tau_\sigma}. \tag{14.1.13}$$

This equation shows that the lasing frequency is neither ω_{TLS} nor ω_R.

For the nontrivial stationary solution, Eqs. (14.1.7)–(14.1.8) give:

$$a_{st} = \frac{e^{i\phi}}{2} \left(\frac{\tau_a}{\tau_D} (D_0 - D_{th}) \right)^{\frac{1}{2}}, \tag{14.1.14}$$

while Eq. (14.1.9) reduces to $(D_{th} - D_0)/\tau_D = 2i\Omega_R \left(a_R^* \sigma - \sigma^* a_R \right) = a_R^* a_R = (D_0 - D_{th})\tau_a / 4\tau_D$ or

$$\sigma_{st} = a_{st} \frac{(\Delta + i/\tau_a)}{\Omega_R} \tag{14.1.15}$$

The dependence

$$a_{st} = \begin{cases} 0 & D_0 < D_{th} \\ \propto \sqrt{D_0 - D_{th}} & D_0 > D_{th} \end{cases} \tag{14.1.16}$$

shows the dependence of the lasing mode amplitude on the incoherent pump power D_0. It is called the Hopf bifurcation and is typical for lasers [27]. Equations (14.1.12) and (14.1.13) determine the lasing threshold D_{th} and lasing frequency ω, respectively.

14.2 The Regime of Convention Laser Without Excitation of Coherent Phonons

The trivial time-independent solution to Eqs. (14.1.2)–(14.1.5) that corresponds to the regime in which coherent oscillations of a, σ, and b are absent has the form:

$$a_{triv} = 0, \tag{14.2.1}$$

$$\sigma_{triv} = 0, \tag{14.2.2}$$

$$D_{triv} = D_0, \tag{14.2.3}$$

$$b_{triv} = \frac{-g(D_0 + 1)}{2\omega_v - i\gamma_v}. \tag{14.2.4}$$

This solution is analogous to the trivial zero-valued solution for a conventional laser, in which the phonon degree of freedom of the active medium molecule is not taken into account. Usually, this solution is stable below the lasing threshold D_{th_opt}. In our case, the trivial solution is characterized by a nonzero time-independent expectation value of the phonon operator b_{triv}, corresponding to a constant displacement of nuclei. It appears for the following reason. When a molecule is excited, its nuclear equilibrium positions change. Therefore, pumping results in nonzero occupation of the excited state with the population D_0 + 1. As a result, nuclei move to new equilibrium positions, and Eq. (14.2.4) determines these positions with respect to the equilibrium position for the ground state. (A similar phenomenon is the Kapitza pendulum. The equilibrium position of the pendulum changes due to high-frequency vibrations of the pendulum suspension point [28].)

It is expected that as the pump rate characterized by D_0 increases, the lasing begins. When $D_0 > D_{th_opt}$, the trivial solution becomes unstable, and a stable self-oscillating solution arises. The computer simulation indeed shows such a transition to the lasing self-oscillating regime. There are still no coherent phonons in this regime, and the coherent part of b, which we denote as b_{ph}, is still equal to zero.

Since we are interested in the stationary behavior of the system, i.e., the behavior at large times, $t \gg \gamma_a^{-1}, \gamma_\sigma^{-1}, \gamma_b^{-1}$, we search for self-oscillating solutions in the following form:

$$a = a_{opt}(D_0)\exp\left(-i\omega_{gen}t\right), \tag{14.2.5}$$

$$\sigma = \sigma_{opt}(D_0)\exp\left(-i\omega_{gen}t\right), \tag{14.2.6}$$

$$D = D_{th_opt}, \tag{14.2.7}$$

$$b = \frac{-g\left(D_{th_opt} + 1\right)}{2\omega_v - i\gamma_v}. \tag{14.2.8}$$

Here, a_{opt} and σ_{opt} are time-independent amplitudes; ω_{gen} and D_{th_opt} are the frequency and the threshold of the laser generation. These four quantities should still be determined. According to Eqs. (14.2.3) and (14.2.7)

$$D = D_0 \quad \text{if} \quad D_0 < D_{th_opt} \quad \text{and} \quad D = D_{th_opt} \quad \text{if} \quad D_0 > D_{th_opt}. \tag{14.2.9}$$

Substituting Eqs. (14.2.5)–(14.2.8) into Eqs. (14.1.2)–(14.1.5) and equating the real and imaginary parts of Eq. (14.1.3) to zero, after some algebra, we obtain the following expression for the population inversion and the self-oscillation frequency:

$$D_{th_opt} = \frac{\left(-\delta_{gen}\Delta_{gen} + \frac{\gamma_\sigma \gamma_a}{4}\right)\left(\omega_v^2 + \frac{\gamma_v^2}{4}\right) - \omega_v g^2 \Delta_{gen}}{\omega_v g^2 \Delta_{gen} + \Omega_R^2\left(\omega_v^2 + \frac{\gamma_v^2}{4}\right)}, \tag{14.2.10}$$

$$\begin{aligned}&\left(\delta_{gen}\gamma_a + \Delta_{gen}\gamma_\sigma\right)\left(\omega_v g^2 \Delta_{gen} + \Omega_R^2\left(\omega_v^2 + \frac{\gamma_v^2}{4}\right)\right)\\ &+\omega_v g^2 \gamma_a\left(-\delta_{gen}\Delta_{gen} + \frac{\gamma_\sigma \gamma_a}{4} + \Omega_R^2\right) = 0,\end{aligned} \tag{14.2.11}$$

where $\Delta_{gen} = \omega_{gen} - \omega_a$ and $\delta_{gen} = \omega_{gen} - \omega_\sigma$. It is important that Eqs. (14.2.10) and (14.2.11) have terms proportional to g^2, resulting in the dependence of the stationary threshold population inversion and the frequency of self-oscillations $\omega_{gen}(g)$ on the Fröhlich constant g. In particular, the frequency of self-oscillations, which appear above the laser threshold, can be rewritten as

$$\omega_\sigma^{(g)} = \omega_\sigma - \frac{\omega_v g^2 \left(D_{th_opt} + 1\right)}{\omega_v^2 + \gamma_v^2/4}, \tag{14.2.12}$$

Remark 14.2 **Effective change in the exciton frequency due to a constant displacement of molecular nuclei in QD under incoherent pumping**. To study the spontaneous emission of a TLS interacting with phonons but not with the EM field, we employ our basis system of equations (14.1.2)–(14.1.5), where we put $\Omega_R = 0$. The trivial stationary solution to this system still has the form:

$$a_{st} = 0, \sigma_{st} = 0, D_{st} = D_0, b_{st} = \frac{-g\left(D_{th_opt} + 1\right)}{2\omega_b - i\gamma_b}.$$

Let us consider the dynamics of small deviations of the QD dipole moment σ from its equilibrium position. Substituting $\sigma = \sigma_{st} + \delta\sigma$, $b = b_{st} + \delta b$, and $D = D_{st} + \delta D$ into the basis system of equations, assuming $\omega_\sigma \gg g$ (this inequality is always satisfied since ω_σ lies in the optical range and g is in the IR range), and implying that the value of δb is small compared to b_{st}, we obtain:

$$d(\delta\sigma)/dt = (-i\omega_\sigma - \gamma_\sigma/2)\delta\sigma - ig\left(b_{st} + b_{st}^\dagger\right)\delta\sigma = \left(-i\omega_\sigma^{(g)} - \gamma_\sigma/2\right)\delta\sigma,$$

where we have introduced the notation for the phonon-induced pump-dependent red frequency shift of the QD eigenfrequency $\omega_\sigma^{(g)}$

(continued)

Remark 14.2 (continued)

$$\omega_\sigma^{(g)} = \omega_\sigma - \frac{\omega_b g^2 (D_0 + 1)}{\omega_b^2 + \gamma_b^2/4},$$

Thus, the oscillations of the exciton dipole moment near the equilibrium position occur not at the exciton eigenfrequency ω_σ but at the shifted frequency $\omega_\sigma + \omega_{sh}$. The shift ω_{sh} is always negative and proportional to the value $D_0 + 1$, which corresponds to the population of the excited state of the exciton at a nonzero pump rate $D_0 > -1$.

Using the notation

$$\omega_\sigma^{(g)} = \omega_\sigma - \left(\omega_v g^2 (D_0 + 1)\right) / \left(\omega_v^2 + \gamma_v^2/4\right) \tag{14.2.13}$$

(see Remark 14.2), we can reduce Eq. (14.2.11) to the form:

$$\omega_{gen} = \frac{\omega_\sigma^{(g)} \gamma_\sigma + \omega_a \gamma_a}{\gamma_\sigma + \gamma_a}.$$

which is valid in the absence of the interaction between phonons (vibrons) and excitons when $\omega_\sigma^{(g)} = \omega_\sigma$; this formula shows that $\omega_{gen} \neq \omega_a$. Equation (14.2.10) for the threshold can be rewritten as

$$D_{th_opt} = D_{0,th} = \frac{\gamma_a \gamma_\sigma}{4\Omega_R^2} \left(1 + \frac{4\left(\omega_a - \omega_\sigma^g\right)^2}{\left(\gamma_a + \gamma_\sigma\right)^2}\right).$$

This equation coincides with the usual expression for the laser threshold, in which ω_σ is replaced with $\omega_\sigma^{(g)}$. Equation (14.2.13) defines the value of the effective transition frequency of an exciton under the influence of incoherent pumping due to the interaction of excitons with an optical phonon.

For the field amplitude in the resonator and the polarization, using Eqs. (14.2.10)–(14.2.11), we can obtain the following expressions (see Eqs. (14.1.7)–(14.1.16)):

$$a_{opt} = \begin{cases} 0 \quad \text{for} \quad D_0 < D_{th_opt}, \\ \sqrt{\dfrac{(\gamma_p + \gamma_D)(D_0 - D_{th_opt})}{2\gamma_a}} \quad \text{for} \quad D_0 > D_{th_opt}, \end{cases}$$

$$\sigma_{opt} = \begin{cases} 0 \quad \text{for} \quad D_0 < D_{th_opt}, \\ \dfrac{i\Delta - \gamma_a/2}{i\Omega_R} \sqrt{\dfrac{(\gamma_p + \gamma_D)}{2\gamma_a}(D_0 - D_{th_opt})} \quad \text{for} \quad D_0 > D_{th_opt}. \end{cases} \tag{14.2.14}$$

Such a behavior corresponds to the Hopf bifurcation at $D_0 = D_{th_opt}$. Though phonons influence the bifurcation process in the regime discussed above, they are not involved in the self-oscillations.

14.3 The Laser Regimes with Excitation of Coherent Phonons

In this section, we show that a further increase in the pump rate may lead to another Hopf bifurcation, resulting in either the generation of coherent phonons or deterministic chaos.

14.3.1 The Resonant Case $\omega_a = \omega_\sigma^{(g)}$: The Second Hopf Bifurcation Phonons

Let us first consider the resonant case $\omega_a = \omega_\sigma^{(g)}$. Now, we have two parameters g and D_0, which determine possible operational regimes of the laser. These regimes can be found by solving Eqs. (14.1.2)–(14.1.5) for $D_0 > D_{th_opt}$. This system of equations can only be solved numerically.

The possible operational regimes on the plane (g, D_0) obtained by computer simulation are shown in Fig. 14.1. One can see that there are two threshold values of the pump rate D_0, which separate different regimes. When the pump rate D_0 is less than the optical threshold D_{th_opt} (shown by the left solid vertical line) determined by Eq. (14.2.10), only trivial solution (14.2.1)–(14.2.4) is stable (the blue area in Fig. 14.1). Note that at a large pump rate, a disruption of the generation occurs. This is shown by the right vertical blue strip in Fig. 14.1. In this region, the generation stops due to an increase in the dissipation rate of the exciton polarization γ_σ with an increase in the pump rate γ_p. When the pump rate becomes as high as $\gamma_p \gg \gamma_D$, γ_{deph}, the dissipation of the polarization becomes so large that laser generation is hindered [29, 30].

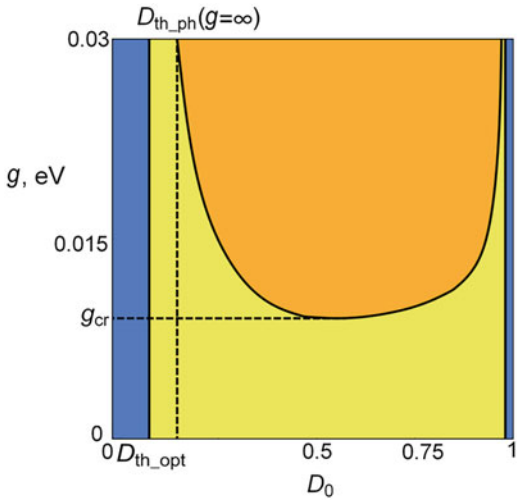

Fig. 14.1 Operational regimes in the plane of parameters (g, D_0). There is no lasing in the blue region ($D_0 < D_{th_opt}(g)$), in which only the trivial solution is stable. In the right blue area, the generation is disrupted by a large pump rate. The yellow region is the self-oscillating laser regime without the excitation of coherent phonons. The orange region shows the regime of self-oscillations of coherent phonons and the periodic-in-time part of the optical field in the resonator. The system parameters are $\Omega_R = 0.01eV$, $\gamma_b = 0.0002eV$, $\gamma_a = 0.001eV$, $\omega_b = 0.01eV$, $\omega_\sigma = 2.4eV$, $\gamma_{deph} = 0.005eV$, and $\gamma_D = 0.001eV$

When $D_0 > D_{th_opt}(g)$, the numerical analysis of Eqs. (14.1.2)–(14.1.5) shows that the trivial solution becomes unstable, and a new self-oscillating solution without coherent phonons arises (see Eq. (14.2.14)). This solution is stable for any g until $D_0 < D_{th_ph}(g = \infty)$ (the yellow region to the left of the dashed vertical line in Fig. 14.1). In this regime, the expectation value of the nuclear displacements due to their coherent vibrations about equilibrium positions is zero, $b_{ph} = 0$. Therefore, despite accounting for the electron-phonon interaction, the laser radiation spectrum contains neither Stokes nor anti-Stokes frequencies. It means that nuclei do not take part in self-oscillation. This is exactly what is usually assumed when the electron-phonon interaction is neglected.

In the region $D_0 > D_{th_ph}(g = \infty)$, there is a curve $D_0 = D_{th_ph}(g)$, the solid curve, which bounds the orange area in Fig. 14.1. In this area, the lasing regime without coherent phonons becomes unstable, and as we show below, a new regime with coherent phonons arises. We also show that this is a new Hopf bifurcation leading to the formation of new self-oscillations at the frequency close to ω_v.

To study the latter regime, it is convenient to present the trial form for the expectation values of the operators $\widehat{a}$, $\widehat{\sigma}$, $\widehat{D}$, and $\widehat{b}$ in the following form:

$$a(t) = \left(a_{opt} + a_{ph}(t)\right) \exp\left(-i\omega_{gen}t\right), \tag{14.2.15}$$

$$\sigma(t) = \left(\sigma_{opt} + \sigma_{ph}(t)\right) \exp\left(-i\omega_{gen}t\right), \tag{14.2.16}$$

$$D(t) = D_{th_opt} + D_{ph}(t), \tag{14.2.17}$$

$$b(t) = \frac{-g\left(D_{th_opt} + 1\right)}{2\omega_v - i\gamma_v} + b_{ph}(t). \tag{14.2.18}$$

Here, we split the amplitudes of $a(t)$, $\sigma(t)$, $D(t)$, and $b(t)$ into the time-independent parts (a_{opt}, σ_{opt}, D_{th_opt}, and $-g(D_{th_opt} + 1)/(2\omega_v - i\gamma_b)$), corresponding to the conventional laser regime (see Eqs. (14.2.5)–(14.2.4)), and the time-dependent parts, $a_{ph}(t)$, $\sigma_{ph}(t)$, $D_{ph}(t)$, and $b_{ph}(t)$ determined by Eqs. (14.2.15)–(14.2.18), forming new nonharmonic self-oscillations with the period:

$$T = 2\pi/\omega_{v,gen}, \tag{14.2.19}$$

where $\omega_{v,\,gen} \equiv 2\pi/T \neq \omega_v$ is the lowest frequency that determines the periodicity of self-oscillations of $a_{ph}(t)$, $\sigma_{ph}(t)$, $D_{ph}(t)$, and $b_{ph}(t)$.

In order to characterize the transition to the self-oscillation with coherent phonons, we average the quantities $|a_{ph}(t)|$, $|\sigma_{ph}(t)|$, $|D_{th}(t)|$, and $|b_{th}(t)|$ over the period of the self-oscillations: $\langle \ldots \rangle = \frac{1}{T}\int_{t_0}^{t_0+T} |\ldots| dt$, where $t_0 \gg \gamma_a^{-1}, \gamma_\sigma^{-1}, \gamma_v^{-1}$ is the time during which the system reaches stationary oscillations and T is the period of new self-oscillations. Figure 14.2 shows the dependence of $\langle |b_{ph}| \rangle$ on the pump rate D_0 for fixed $g > g_{cr}$. This dependence behaves like $\sim \sqrt{D_0 - D_{th_ph}}$, which shows that at the second threshold D_{th_ph} (the vertical dashed line in Fig. 14.1), another Hopf bifurcation occurs.

In the new regime, the spectrum of the self-oscillations is not characterized by a single frequency $\omega_{v,\,gen}$. These self-oscillations can be presented as the Fourier series $a_{ph}(t) = \sum_n a_n \exp\left(-i\left(\omega_\sigma^{(g)} + \omega_{v,gen}n\right)t\right)$, where the coefficients a_n are time-

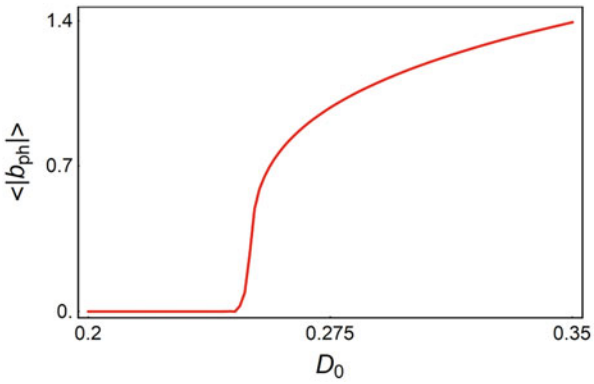

Fig. 14.2 The dependence of $\langle |b_{ph}| \rangle$ on the pump rate D_0 for fixed $g = 0.015\text{eV} > g_{cr}$. Other parameters are the same as in Fig. 14.1

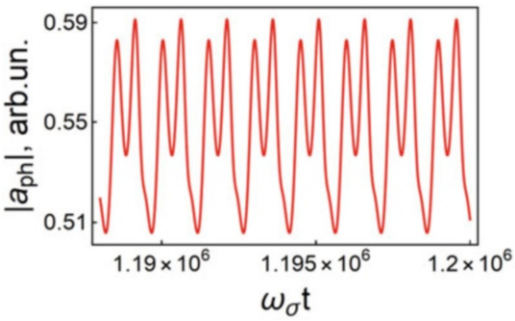

Fig. 14.3 Dependencies of the resonator electric field amplitude $|a_{ph}(t)|$ on time. $D_0 = 0.6$ and $g = 0.019\,eV$. Other parameters are the same as in Fig. 14.1

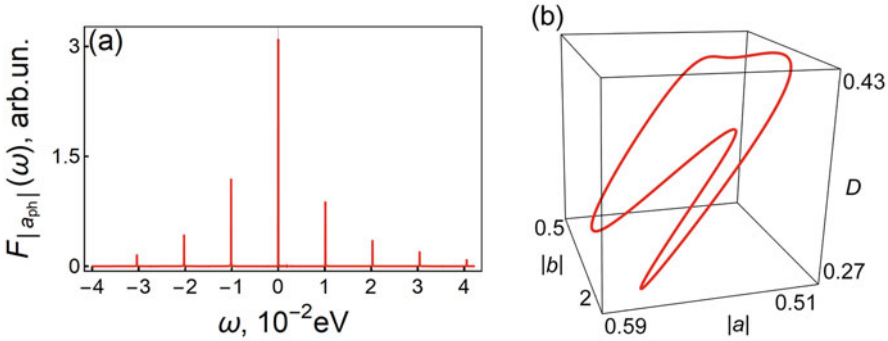

Fig. 14.4 (**a**) The discreet spectrum $F_{|a_{ph}|}(\omega)$ obtained by computer simulation. (**b**) The closed cycle of self-oscillation in the space of variables $|a(t)|$, $|b(t)|$, and $|D(t)|$. The parameters are the same as in Fig. 14.3 and correspond to the black point in Fig. 14.5a

independent. The sidelobes of $a_{ph}(t)$ appear due to the cascade effect of Raman lasing discussed in Sect. 13.3. Indeed, since we are working above the lasing threshold, the number of coherent vibrons is much greater than unity. Consequently, the Stoke and anti-Stokes signals are also coherent. If the corresponding frequencies lie inside the line of lasing on the main lasing frequency $\omega_\sigma^{(g)}$ $(n = 0)$, then the Stoke and anti-Stokes signals $(n = \pm 1)$ also start lasing.

Using computer simulation, we obtain the spectrum of $|a_{ph}(t)|$ shown in Fig. 14.3. The spectrum of oscillations of $|a_{ph}(t)|$ is determined by the equality:

$$F_{|a_{ph}|}(\omega) = \frac{1}{T}\int_{t_0}^{t_0+T} dt \exp(i\omega t)\left|a_{ph}(t)\right|, \tag{14.2.20}$$

as shown in Fig. 14.4a. This spectrum with high accuracy consists of picks at frequencies $\omega = n\omega_{v,\,gen}$, where n is an integer [20, 31]. As a consequence, on the right-hand side of the equation for the dynamics of vibrons, the external field with

the spectrum $\sim \sum_n c_n \exp\left(-i\left(\omega_{v,gen} n\right)t\right)$ appears. The dynamics of vibrons is illustrated in Fig. 14.4b, which shows the projection of the closed cycle of self-oscillations on the space $|a|$, $|b|$, and D. One can see that the system dynamics is presented by a closed curve, which is the manifestation of regime periodicity.

The appearance of $b_{ph} \neq 0$ implies the emergence of coherent phonons. The latter does not appear in spontaneous Raman scattering, even if the incident field is coherent. Thus, this fact cannot be attributed to the Raman scattering of the laser mode. This is confirmed by the computer experiment. Figure 14.1 shows that the threshold for a coherent harmonic laser mode D_{th_opt} and the threshold D_{th_ph} for the appearance of coherent phonons are different.

Usually, the coherent phonons arise in systems in CARS or after the onset of Raman lasing. As discussed in Sect. 13.4, in CARS, the appearance of coherent phonons is associated with the resonant excitation of optical phonons at the frequency difference of *two* incident *coherent* waves. In a conventional laser and in our scheme, the pumping is *incoherent*, and the only coherent wave is the resonator mode above the laser threshold D_{th_opt}. This is clearly not enough for the CARS mechanism to lead to the excitation of coherent phonons.

14.3.2 Nonresonant Case $\omega_a \neq \omega_\sigma^{(g)}$

Now, we consider the operational regimes in the case of $\omega_a \neq \omega_\sigma^{(g)}$. For conventional lasers, in which electron-phonon interaction is negligible ($g = 0$), the optimal condition for lasing is matching the resonator frequency ω_a with the transition frequency ω_σ. When this happens, the laser threshold is minimal. With an increase in the frequency difference $|\omega_a - \omega_\sigma|$, the lasing threshold D_{th_opt} increases. There is the value of $|\omega_a - \omega_\sigma|$, at which D_{th_opt} becomes greater than D_0. Then, the pump rate is not sufficient to start lasing, and self-oscillation does not appear. The trivial solution becomes stable again; consequently, the lasing does not occur.

As computer simulation shows, similar behavior is observed at $g \neq 0$. In this case, however, the role of ω_σ is played by $\omega_\sigma^{(g)}$. At a fixed pump rate $D_0 > D_{th_opt}$, with an increase in the difference $\left|\omega_a - \omega_\sigma^{(g)}\right|$, the lasing threshold also grows, and sooner or later, this should lead to the suppression of lasing. By computer simulation, for each g we can determine the interval of frequencies ω_a, where lasing is observed. The lasing interval for a conventional laser now transforms into the lasing corridor on the plane (ω_a, g) (see Fig. 14.5).

The results of the computer simulation are shown in Fig. 14.5. On the plane of the parameters ω_a and g, the dependence $\omega_\sigma^{(g)}(g)$ at fixed $D_0 > D_{th_opt}$ is shown by the solid blue line. The corridor of parameters for which the lasing is observed (the lasing corridor) is bounded by the dotted lines. Outside this corridor, only the trivial solution is stable, and the system does not lase. Below, we deal with the parameters inside the lasing corridor.

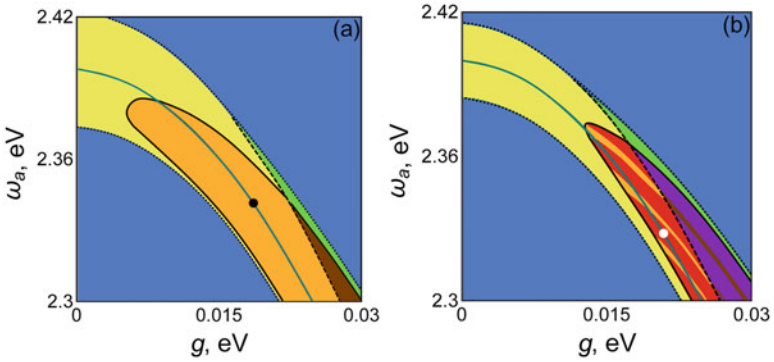

Fig. 14.5 Operational regimes of lasing in the parameter plane (ω_a, g); (**a**) $\gamma_\sigma = 0.005eV$ and (**b**) $\gamma_\sigma = 0.002eV$. In the blue areas, lasing is absent; the conventional lasing regime occurs in the yellow area; the operational regime with coherent phonons occupies the orange area; the regime of the chaotic operation occurs in the red area; the area where both trivial and common lasing regimes are stable is colored in green (yellow + blue); the area in which both the common laser regime and the regime with coherent phonons are stable is colored in brown (orange + blue); finally, the area in which both trivial and chaotic solutions are stable is colored in purple (red + blue). The system parameters are $D_0 = 0.6$, $\Omega_R = 0.01\ \ eV$, $\gamma_v = 0.0002\ \ eV$, $\gamma_a = 0.001\ \ eV$, $\omega_v = 0.01\ \ eV$, $\omega_\sigma = 2.4\ \ eV$, $\gamma_D = 0.001\ \ eV$, and $\gamma_p = 0.004\ \ eV$

Inside the lasing corridor, a coherent self-oscillation of phonons in the active medium may occur simultaneously with the self-oscillation of the EM field in the resonator. In Fig. 14.5, the region in which coherent phonons are excited is bounded by the solid black curve. In this figure, the stable solutions with coherent phonons belong to the orange area.

Usually, at large times, the system dynamics is uniquely determined by the external parameters $\{\omega_a, g, D_0\}$ and is independent of initial conditions $\{a, \sigma, D, b\}_{t=0}$. The most intriguing property of this system is that there is an area in which two solutions corresponding to different physical regimes are stable. In Fig. 14.5, this area lies between the upper dotted line and the dashed line: in the green area, the trivial solution and the periodic harmonic solution are stable, while in the brown area, the trivial and periodic nonharmonic solutions are stable. Thus, for different initial values $\{a, \sigma, D, b\}_{t=0}$, with time increase, the system arrives at a different stationary state. For example, in the green area, for the initial conditions close to the trivial solution, the system does not begin lasing with time. If the initial conditions are far from the trivial solution, at large times, the conventional laser self-oscillation mode occurs.

It should be noted that each point in Fig. 14.5 corresponds to a particular system having a specific resonator and active material. The resonator frequency ω_a and the Fröhlich interaction constant g are plotted along the axes; the Rabi frequency and the pump rate are fixed.

14.3.3 The Transition from Self-Oscillations with Coherent Phonons to Chaos

If the electron-phonon interaction is not present in the laser system that we consider, the chaotic regime does not arise [32]. Therefore, there is no reason to expect a transition of the considered system to chaos. Nonetheless, it is not so. The electron-phonon interaction significantly changes the laser dynamics. Namely, if the rate of the exciton dephasing γ_σ is reduced (but the inequality $\gamma_a < \gamma_\sigma$ still holds), then areas of chaos appear in the region where coherent phonons may arise. Such a decrease in γ_σ can be achieved, for example, by lowering the temperature. For such a case, various operational regimes are shown in Fig. 14.5b.

Figure 14.6a, b shows time dynamics $|\sigma(t)|$ and the spectrum $F_{|\sigma|}(\omega)$, respectively. The parameters g, D_0, and ω_a correspond to the white point in Fig. 14.5b. With the accuracy of our computer simulation, which is about 10^{-7}eV, *all* frequencies are present in the spectrum. Such a spectrum drastically differs from the discrete spectrum observed for self-oscillations (Fig. 14.4a). This is characteristic for a chaotic regime.

To summarize the results discussed in this chapter, we can say that the electron-phonon interaction may dramatically change the behavior of a laser [18]. It may lead to new regimes of laser dynamics which do not exist in conventional lasers. Moreover, it may convert a laser into a generator of coherent optical phonons. Finally, this interaction may lead to the dependence of the laser state on initial conditions, i.e., the initial values of the resonator field, the active medium polarization, the population inversion, and the phonon amplitude govern which regime is realized.

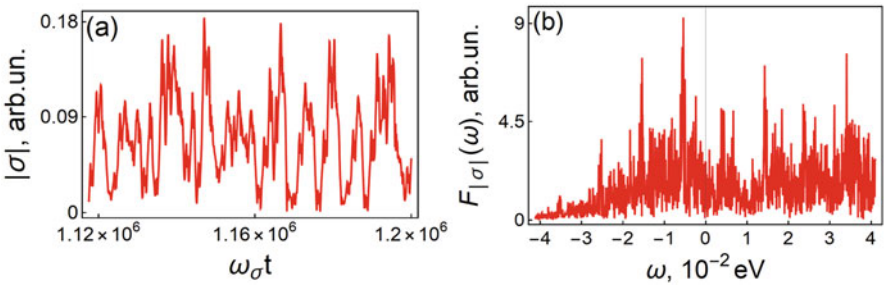

Fig. 14.6 (**a**) Time dynamics of $|\sigma(t)|$ and (**b**) its spectrum $F_{|\sigma|}(\omega)$ corresponding to the white point in Fig. 14.5b, in which the chaotic regime is realized. $g = 0.0214\ eV$ and $\omega_a = 2.327\ eV$; other parameters are the same as in Fig. 14.5

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Chapter 15
Conclusion

In this book, the phenomena of inelastically scattered light on molecules are associated with the excitation of the vibrational degrees of freedom of the molecule nuclei. The developed approach is based on the original qualitative ideas of classical physics—the modulation of the oscillation of the molecular dipole moment by vibrations of molecular nuclei.

It is shown that this excitation is due to an indirect nonlinear interaction between electronic and nuclear subsystems of a molecule. This interaction can be described in terms of the Fröhlich Hamiltonian. The well-known effects of Raman scattering, such as CARS, CERS, SECARS, and SRS, are considered from a unified standpoint of quantum mechanics. The quantum-mechanical approach based on the Heisenberg-Langevin operator equations has been consistently developed from the first principles. Within the framework of the developed approach, it was possible to answer a number of questions that do not have an answer in the framework of the traditional theory of dispersion based on the introduction of virtual levels. In particular, an explanation is given for the coherent properties of various responses. This includes the explanations of the coherence of Rayleigh scattering, the coherence of Raman scattering generated by a single coherent wave, and the coherence of the Stokes and anti-Stokes signals generated by two coherent waves.

Attention is drawn to the possibility of enhancing the Raman responses due to the excitation of vibrational oscillations of the nuclei of a molecule. It is an extra way, in addition to the gain in SERS. In the long run, it is necessary to consider the enhancement of the oscillations of nuclei in molecules due to the interaction with the phonons of both the substrate and the analyte in the crystalline state.

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Chapter 16
Problems for Part II

Problem 2.1
Solve the problem:

$$\frac{dy(t)}{dt} = \gamma y(t) + C(t) \tag{16.1.1}$$

Solution
The solution to Eq. (16.1.1) has the form $y_0(t)$+$y_C(t)$, where $y_0(t)$ is the general solution to Eq. (16.1.1) with $C(t) \equiv 0$:

$$\frac{dy_0(t)}{dt} = \Gamma y_0(t), \tag{16.1.2}$$

and $y_C(t)$ is a partial solution to Eq. (16.1.1).

The general solution to Eq. (16.1.2) is $y_0(t) = y_{C=0} \exp(\Gamma t)$, where $y_{C=0}$ is any constant. The partial solution to Eq. (16.1.1) is searched in the form:

$$y_C(t) = y_{C\neq 0}(t) \exp(\Gamma t) \tag{16.1.3}$$

where it is assumed that $y_{C\neq 0}(t)$ is an unknown function and that at $y_{C=0} = 1$, $y_{C\neq 0}(0) = y_{C=0}(0)$.

Substituting (16.1.3) into Eq. (16.1.1), we obtain:

$$\frac{dy_C(t)}{dt} = \exp(\Gamma t)\frac{dy_{C\neq 0}(t)}{dt} + \Gamma y_{C\neq 0}(t)\exp(\Gamma t) = \Gamma y_{C\neq 0}(t)\exp(\Gamma t) + C(t)$$

or

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$$\frac{dy_{C\neq 0}(t)}{dt} = \exp(-\Gamma t)C(t).$$

Taking into account that the solution to the latter equation is

$$y_{C\neq 0}(t) = \int_0^t \exp(-\gamma t')C(t')dt',$$

we arrive at the following partial solution to

$$y_C(t) = \exp(\Gamma t)\int_0^t \exp(-\Gamma t')C(t')dt' \tag{16.1.4}$$

Note that $C(t)$ can be both continuous function and stochastic function describing noise. Also, the solution (16.1.4) is valid if $y(t)$ is a quantum mechanical operator.

Problem 2.2
Find the radiation spectrum of a Raman-active molecule. In the first two orders of the perturbation theory, the dipole moment of such a molecule is described by Eqs. (11.1.31) and (11.1.33) of Part II:

$$\sigma(t) = \sigma_1(t) + \sigma_2(t),$$

$$\widehat{\sigma}_1(t) = \widehat{I}\frac{1}{2}\frac{\Omega_{ext}}{(\omega_{ext}-\omega_\sigma)}e^{-i\omega_{ext}t}, \qquad \widehat{\sigma}_1^\dagger(t) = \widehat{I}\frac{1}{2}\frac{\Omega_{ext}}{(\omega_{ext}-\omega_\sigma)}e^{i\omega_{ext}t} \tag{16.2.1}$$

$$\begin{aligned}\widehat{\sigma}_2(t) &= e^{-(i\omega_\sigma+\gamma_\sigma)t}\int_0^t dt' e^{(i\omega_\sigma+\gamma_\sigma)t'}\frac{-ig\Omega e^{-i\omega_{ext}t'}}{2(\omega_{ext}-\omega_\sigma)}\\ &\times\int_0^{t'} dt'' e^{-\gamma_v(t'-t'')}\left[e^{i\omega_v(t'-t'')}\widehat{F}_b^\dagger(t'') + e^{-i\omega_v(t'-t'')}\widehat{F}_b(t'')\right]\\ &= e^{-(i\omega_\sigma+\gamma_\sigma)t}\frac{-ig\Omega_{ext}}{2(\omega_{ext}-\omega_\sigma)}\int_0^t dt' e^{(i\omega_\sigma+\gamma_\sigma)t'}e^{-i\omega_{ext}t'}\\ &\times\int_0^{t'} dt'' e^{-\gamma_v(t'-t'')}\left[e^{i\omega_v(t'-t'')}\widehat{F}_b^\dagger(t'') + e^{-i\omega_v(t'-t'')}\widehat{F}_b(t'')\right],\end{aligned} \tag{16.2.2}$$

$$\begin{aligned}\widehat{\sigma}_2^{\dagger}(t) &= e^{(i\omega_\sigma-\gamma_\sigma)t}\int\limits_0^t dt' \mathrm{e}^{(-i\omega_\sigma+\gamma_\sigma)t'}\frac{ig\Omega e^{i\omega_{ext}t'}}{\omega_{ext}-\omega_\sigma}\\ &\times\int\limits_0^{t'} dt'' e^{-\gamma_v(t'-t'')}\left[e^{i\omega_v(t'-t'')}\widehat{F}_b^{\dagger}(t'')+e^{-i\omega_v(t'-t'')}\widehat{F}_b(t'')\right]\\ &= e^{(i\omega_\sigma-\gamma_\sigma)t}\frac{ig\Omega_{ext}}{(\omega_{ext}-\omega_\sigma)}\int\limits_0^t dt' \mathrm{e}^{(-i\omega_\sigma+\gamma_\sigma)t'}e^{i\omega_{ext}t'}\\ &\times\int\limits_0^{t'} dt'' e^{-\gamma_v(t'-t'')}\left[e^{i\omega_v(t'-t'')}\widehat{F}_b^{\dagger}(t'')+e^{-i\omega_v(t'-t'')}\widehat{F}_b(t'')\right],\end{aligned} \tag{16.2.3}$$

Solution

The expressions (16.2.1)–(16.2.3) enable us to calculate the emission spectrum. According to Wiener-Khintchine theorem, the spectrum is determined by the two-time correlation function of the dipole moment, which is proportional to $\left\langle\widehat{\sigma}^{\dagger}(t+\tau)\widehat{\sigma}(t)\right\rangle$ (for the derivation, see Sect. 3.4.2). For this correlator, we have:

$$\begin{aligned}\left\langle\widehat{\sigma}^{\dagger}(t+\tau)\widehat{\sigma}(t)\right\rangle &= \left\langle\left(\widehat{\sigma}_1^{\dagger}(t+\tau)+\widehat{\sigma}_2^{\dagger}(t+\tau)\right)(\widehat{\sigma}_1(t)+\widehat{\sigma}_2(t))\right\rangle\\ &= \left\langle\widehat{\sigma}_1^{\dagger}(t+\tau)\widehat{\sigma}_1(t)\right\rangle+\left\langle\widehat{\sigma}_1^{\dagger}(t+\tau)\widehat{\sigma}_2(t)\right\rangle+\left\langle\widehat{\sigma}_2^{\dagger}(t+\tau)\widehat{\sigma}_1(t)\right\rangle+\left\langle\widehat{\sigma}_2^{\dagger}(t+\tau)\widehat{\sigma}_2(t)\right\rangle\end{aligned} \tag{16.2.4}$$

Note that from Eq. (16.2.3), it follows that the second and the third terms on the right-hand side of Eq. (16.2.4) have the terms, which are linearly dependent on $\left\langle\widehat{IF}_b(\tau')\right\rangle=\left\langle\widehat{F}_b(\tau')\right\rangle$ or $\left\langle\widehat{IF}_b^{\dagger}(\tau')\right\rangle=\left\langle\widehat{F}_b^{\dagger}(\tau')\right\rangle$. According to general properties of thermal noises (see Problem 1.10 in Part I), $\left\langle\widehat{F}_b^{\dagger}(t)\right\rangle=\left\langle\widehat{F}_b(t)\right\rangle=0$; thus, the second and third terms in right-hand side of Eq. (16.2.4) are zero. Thus, we have:

$$\left\langle\widehat{\sigma}^{\dagger}(t+\tau)\widehat{\sigma}(t)\right\rangle=\left\langle\widehat{\sigma}_1^{\dagger}(t+\tau)\widehat{\sigma}_1(t)\right\rangle+\left\langle\widehat{\sigma}_2^{\dagger}(t+\tau)\widehat{\sigma}_2(t)\right\rangle \tag{16.2.5}$$

Further, from Eq. (16.2.1), it follows that

$$\left\langle\widehat{\sigma}_1^{\dagger}(t+\tau)\widehat{\sigma}_1(t)\right\rangle=\left\langle\widehat{1}\frac{\Omega}{2(\omega_{ext}-\omega_\sigma)}e^{i\omega_{ext}(t+\tau)}\widehat{1}\frac{\Omega}{2(\omega_{ext}-\omega_\sigma)}e^{-i\omega_{ext}t}\right\rangle=\frac{\Omega^2}{4(\omega_{ext}-\omega_\sigma)^2}e^{i\omega_{ext}\tau} \tag{16.2.6}$$

Thus, in the first order, we have pure harmonic oscillations of the two-time correlator.

The second term on the right-hand side of Eq. (16.2.5) can be calculated using the explicit expression for $\widehat{\sigma}_2$ (Eq. (16.2.3)). The result is

$$\left\langle \widehat{\sigma}_2^{\dagger}(t+\tau)\widehat{\sigma}_2(t)\right\rangle = \frac{g^2\Omega^2 e^{(i\omega_\sigma-\gamma_\sigma)\tau}e^{-2\gamma_\sigma t}}{4(\omega_{ext}-\omega_\sigma)^2}$$
$$\times\left[\int_0^{t+\tau} d\tau_1 e^{(-i\omega_b-\gamma_b)\tau_1}e^{(i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1}\int_0^{\tau_1} d\tau_2 e^{(i\omega_b+\gamma_b)\tau_2}\right.$$
$$\times\int_0^{t} d\tau_1' e^{(-i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1'}e^{(i\omega_b-\gamma_b)\tau_1'}\int_0^{\tau_1'} d\tau_2' e^{(-i\omega_b+\gamma_b)\tau_2'}\left\langle \widehat{F}_b(\tau_2)\widehat{F}_b^{\dagger}(\tau_2')\right\rangle$$
$$+\int_0^{t+\tau} d\tau_1 e^{(i\omega_b-\gamma_b)\tau_1}e^{(i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1}\int_0^{\tau_1} d\tau_2 e^{(-i\omega_b+\gamma_b)\tau_2}$$
$$\left.\times\int_0^{t} d\tau_1' e^{(-i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1'}e^{(-i\omega_b-\gamma_b)\tau_1'}\int_0^{\tau_1'} d\tau_2' e^{(i\omega_b+\gamma_b)\tau_2'}\left\langle \widehat{F}_b^{\dagger}(\tau_2)\widehat{F}_b(\tau_2')\right\rangle\right] \tag{16.2.7}$$

Taking into account that
$\left\langle \widehat{F}_b^{\dagger}(t_1)\widehat{F}_b(t_2)\right\rangle = \overline{n}_v\delta(t_1-t_2)$, $\left\langle \widehat{F}_b(t_1)\widehat{F}_b^{\dagger}(t_2)\right\rangle = (\overline{n}_v+1)\delta(t_1-t_2)$ (see Eq. (3.1.5) of Part I)
we obtain:

$$\left\langle \widehat{\sigma}_2^{\dagger}(t+\tau)\widehat{\sigma}_2(t)\right\rangle = \frac{g^2\Omega^2}{4(\omega_{ext}-\omega_\sigma)^2}e^{(i\omega_\sigma-\gamma_\sigma)\tau}e^{-2\gamma_\sigma t}2\gamma_b(\overline{n}_v+1)$$
$$\times\int_0^{t+\tau} d\tau_1 e^{(i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1}e^{(-i\omega_b-\gamma_b)\tau_1}\int_0^{\tau_1} d\tau_2 e^{(i\omega_b+\gamma_b)\tau_2}\int_0^{t} d\tau_1' e^{(-i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1'}e^{(i\omega_b-\gamma_b)\tau_1'}$$
$$\int_0^{\tau_1'} d\tau_2' e^{(-i\omega_b+\gamma_b)\tau_2'}\delta(\tau_2-\tau_2')+\frac{g^2\Omega^2 e^{(i\omega_\sigma-\gamma_\sigma)\tau}e^{-2\gamma_\sigma t}2\gamma_b\overline{n}_v}{4(\omega_{ext}-\omega_\sigma)^2}$$
$$\times\int_0^{t+\tau} d\tau_1 e^{(i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1}e^{(i\omega_b-\gamma_b)\tau_1}\int_0^{\tau_1} d\tau_2 e^{(-i\omega_b+\gamma_b)\tau_2}$$
$$\int_0^{t} d\tau_1' e^{(-i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1'}e^{(-i\omega_b-\gamma_b)\tau_1'}\int_0^{\tau_1'} d\tau_2' e^{(i\omega_b+\gamma_b)\tau_2'}\delta(\tau_2-\tau_2')$$
$$=\frac{g^2\Omega^2 e^{(i\omega_\sigma-\gamma_\sigma)\tau}e^{-2\gamma_\sigma t}2\gamma_b(\overline{n}_v+1)}{4(\omega_{ext}-\omega_\sigma)^2}\int_0^{t+\tau} d\tau_1 e^{(i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1}e^{(-i\omega_b-\gamma_b)\tau_1}$$

$$\int_0^t d\tau_1' e^{(-i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1'} e^{(i\omega_b-\gamma_b)\tau_1'} \int_0^{\tau_1'} d\tau_2' e^{2\gamma_b\tau_{22}'} + \frac{g^2\Omega^2 e^{(i\omega_\sigma-\gamma_\sigma)\tau} e^{-2\gamma_\sigma t} 2\gamma_b \overline{n}_v}{4(\omega_{ext}-\omega_\sigma)^2}$$

$$\int_0^{t+\tau} d\tau_1 e^{(i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1} e^{(i\omega_b-\gamma_b)\tau_1} \int_0^t d\tau_1' e^{(-i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1'} e^{(-i\omega_b-\gamma_b)\tau_1'} \int_0^{\tau_1'} d\tau_2' e^{2\gamma_b\tau_2'}$$

$$= \frac{g^2\Omega^2 e^{(i\omega_\sigma-\gamma_\sigma)\tau} e^{-2\gamma_\sigma t} 2\gamma_b(\overline{n}_v+1)}{4(\omega_{ext}-\omega_\sigma)^2} \frac{e^{(i(\omega_{ext}-\omega_\sigma-\omega_b)+(\gamma_\sigma-\gamma_b))(t+\tau)}-1}{i(\omega_{ext}-\omega_\sigma-\omega_b)+(\gamma_\sigma-\gamma_b)}$$

$$\int_0^t d\tau_1' e^{(-i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1'} e^{(i\omega_b-\gamma_b)\tau_1'} \frac{e^{2\gamma_b\tau_1{}'}-1}{2\gamma_b}$$

$$+ \frac{g^2\Omega^2 e^{(i\omega_\sigma-\gamma_\sigma)\tau} e^{-2\gamma_\sigma t} 2\gamma_b \overline{n}_v}{4(\omega_{ext}-\omega_\sigma)^2} \frac{e^{(i(\omega_{ext}-\omega_\sigma+\omega_b)+(\gamma_\sigma-\gamma_b))(t+\tau)}-1}{i(\omega_{ext}-\omega_\sigma+\omega_b)+(\gamma_\sigma-\gamma_b)}$$

$$\int_0^t d\tau_1' e^{(-i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau_1'} e^{(-i\omega_b-\gamma_b)\tau_1'} \frac{e^{2\gamma_b\tau_1{}'}-1}{2\gamma_b}$$

$$= \frac{g^2\Omega^2 e^{(i\omega_\sigma-\gamma_\sigma)\tau} e^{-2\gamma_\sigma t}(\overline{n}_v+1)}{4(\omega_{ext}-\omega_\sigma)^2} \left[\frac{e^{(i(\omega_{ext}-\omega_\sigma-\omega_b)+(\gamma_\sigma-\gamma_b))(t+\tau)}-1}{i(\omega_{ext}-\omega_\sigma-\omega_b)+(\gamma_\sigma-\gamma_b)}\right]$$

$$\left[\frac{e^{(-i(\omega_{ext}-\omega_\sigma-\omega_b)+(\gamma_\sigma+\gamma_b))t}-1}{-i(\omega_{ext}-\omega_\sigma-\omega_b)+(\gamma_\sigma+\gamma_b)}\right] + \frac{g^2\Omega^2 e^{(i\omega_\sigma-\gamma_\sigma)\tau} e^{-2\gamma_\sigma t}\overline{n}_v}{4(\omega_{ext}-\omega_\sigma)^2}$$

$$\left[\frac{e^{(i(\omega_{ext}-\omega_\sigma+\omega_b)+(\gamma_\sigma-\gamma_b))(t+\tau)}-1}{i(\omega_{ext}-\omega_\sigma+\omega_b)+(\gamma_\sigma-\gamma_b)}\right]\left[\frac{e^{(-i(\omega_{ext}-\omega_\sigma+\omega_b)+(\gamma_\sigma+\gamma_b))t}-1}{-i(\omega_{ext}-\omega_\sigma+\omega_b)+(\gamma_\sigma+\gamma_b)}\right]$$

$$= \frac{g^2\Omega^2}{4(\omega_{ext}-\omega_\sigma)^4}(\overline{n}_v+1)e^{(i(\omega_{ext}-\omega_b)-\gamma_b)\tau} + \frac{g^2\Omega^2}{4(\omega_{ext}-\omega_\sigma)^4}\overline{n}_v e^{(i(\omega_{ext}+\omega_b)-\gamma_b)\tau} \tag{16.2.8}$$

Throughout the problem, we suppose that the detuning $|\omega_{ext} - \omega_\sigma|$ is much larger than all dissipation rates γ_σ, γ_b.

The sum of Eqs. (16.2.6) and (16.2.8) gives the total two-time correlation function. It can be presented in more convenient form if we introduce the following notations: $S = \Omega/2(\omega_{ext} - \omega_\sigma)$ and $A_{St} = A_{aSt} = g^2/(\omega_{ext} - \omega_\sigma)^2$. The meaning of S is the Rayleigh response of the TLS on a coherent field (see Eqs. (3.4.41) and (3.4.33) Part I). Using these notations and summing Eqs. (16.2.6) and (16.2.8), we obtain:

$$\left\langle \widehat{\sigma}^\dagger(t+\tau)\widehat{\sigma}(t)\right\rangle = |S|^2\left[e^{i\omega_{ext}\tau} + A_{St}(1+n_v)e^{(i(\omega_{ext}-\omega_b)-\gamma_b)\tau} + A_{aSt}n_v e^{(i(\omega_{ext}+\omega_b)-\gamma_b)\tau}\right] \tag{16.2.9}$$

Problem 2.3
Derive Eq. (12.2.32) for the two-time correlation function of the operator $\widehat{a}$.

Solution
First, we start with the Eqs. (12.2.27)–(12.2.28) from the main text:

$$d\widehat{\sigma}_2/dt + (-i\omega_\sigma - \gamma_\sigma)\widehat{\sigma}_2 = -i\Omega_{Rpl}\widehat{a}_2$$
$$-2ig\widehat{\sigma}_1 \,\mathrm{Re}\left(\int_0^t d\tau \exp(-(i\omega_b + \gamma_b)(t-\tau))\widehat{F}_b(\tau)\right) \tag{16.3.1}$$
$$d\widehat{a}_2/dt + (i\omega_a + \gamma_a)\widehat{a}_2 + i\Omega_{R\,pl}\widehat{\sigma}_2 = 0 \tag{16.3.2}$$

Since we use the perturbation theory, in the right-hand side of Eq. (16.3.1), we should neglect the term proportional to a_2 and take into account only the term proportional to $\widehat{\sigma}_1$. Further, we substitute $\widehat{\sigma}_1$ with $S_{SERS}e^{-i\omega_{ext}t}\widehat{I}$ from Eq. (12.2.22) of the main text. As a result, from Eq. (16.3.1) we obtain:

$$d\widehat{\sigma}_2/dt + (-i\omega_\sigma - \gamma_\sigma)\widehat{\sigma}_2 =$$
$$-igS_{SERS}e^{-i\omega_{ext}t}\left(\int_0^t d\tau e^{(-i\omega_b-\gamma_b)(t-\tau)}\widehat{F}_b(\tau) + \int_0^t d\tau e^{(i\omega_b-\gamma_b)(t-\tau)}\widehat{F}_b^\dagger(\tau)\right) \tag{16.3.3}$$

where $S_{SERS} = \frac{\Omega_{R\,pl}}{(\omega_{ext}-\omega_\sigma)}\,\frac{\alpha\Omega}{2(\omega_{ext}-\omega_a+i\gamma_a)}$. Formally, this equation is equivalent to Eq. (11.1.30) of the main text up to the replacement S_{SERS} to $\frac{\Omega}{2(\omega_{ext}-\omega_\sigma)}$. Thus, the solution to Eq. (16.3.3) coincides with the solution of Eq. (11.1.30), i.e., Eq. (16.2.7), up to the replacement of $\frac{\Omega}{2(\omega_{ext}-\omega_\sigma)}$ to S_{SERS}:

$$\sigma_2(t) = -igS_{SERS}e^{-(i\omega_\sigma+\gamma_\sigma)t}\int_0^t d\tau e^{(-i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau}e^{(i\omega_b-\gamma_b)\tau}\int_0^\tau d\tau' e^{(-i\omega_b+\gamma_b)\tau'}\widehat{F}_b^\dagger(\tau')$$
$$+(-ig)S_{SERS}e^{-(i\omega_\sigma+\gamma_\sigma)t}\int_0^t d\tau e^{(-i(\omega_{ext}-\omega_\sigma)+\gamma_\sigma)\tau}e^{(-i\omega_b-\gamma_b)\tau}\int_0^\tau d\tau' e^{(i\omega_b+\gamma_b)\tau'}\widehat{F}_b(\tau') \tag{16.3.4}$$

We can integrate Eq. (16.3.2) and, for the stationary behavior, obtain the following expression:

$$a_2(t) = -i\Omega_{Rpl}\int_0^t d\tau e^{(i\omega_a-\gamma_a)(t-\tau)}\sigma_2(\tau) \tag{16.3.5}$$

where $\sigma_2(t)$ is the known function on time (16.3.4).

Equation (16.3.5) allows us to reduce calculation of the two-time correlators $\langle a_2(t+\tau)a_2(t)\rangle$ to the correlator $\langle\widehat{\sigma}_2(t+\tau)\widehat{\sigma}_2(t)\rangle$:

$$\left\langle a_2^{\dagger}(t+\tau)a_2(t)\right\rangle = \Omega_{Rpl}^2 e^{(i\omega_a-\gamma_a)(t+\tau)}e^{(-i\omega_a-\gamma_a)t}\int\limits_0^{t+\tau} d\tau_1 e^{(-i\omega_a+\gamma_a)\tau_1}\int\limits_0^{t} d\tau_2 e^{(i\omega_a+\gamma_a)\tau_2}\left\langle\sigma_2^{\dagger}(\tau_1)\sigma_2(\tau_2)\right\rangle \tag{16.3.6}$$

We can find the two-time correlator $\langle\sigma_2(\tau_1)\sigma_2(\tau_2)\rangle$ from Eq. (16.2.8), by substituting $\Omega^2/4(\omega_{ext}-\omega_\sigma)^2$ with S_{SERS}^2:

$$\left\langle\widehat{\sigma}_2^{\dagger}(\tau_1)\widehat{\sigma}_2(\tau_2)\right\rangle = \frac{g^2S_{SERS}^2}{(\omega_{ext}-\omega_\sigma)^2}(\overline{n}_v+1)e^{(i(\omega_{ext}-\omega_b)-\gamma_b)(\tau_1-\tau_2)} + \frac{g^2S_{SERS}^2}{(\omega_{ext}-\omega_\sigma)^2}\overline{n}_v e^{(i(\omega_{ext}+\omega_b)-\gamma_b)(\tau_1-\tau_2)} \tag{16.3.7}$$

Now we should substitute Eq. (16.3.7) into Eq. (16.3.6). Let us first consider the term proportional to $\exp[(i(\omega_{ext}-\omega_b)-\gamma_b)(\tau_1-\tau_2)]$ in the right-hand side of expression (16.3.7):

$$\Omega_{Rpl}^2 e^{(i\omega_a-\gamma_a)(t+\tau)}e^{(-i\omega_a-\gamma_a)t}\frac{g^2|S_{SERS}|^2}{(\omega_{ext}-\omega_\sigma)^2}(\overline{n}_v+1)\int\limits_0^{t+\tau} d\tau_1 e^{(-i\omega_a+\gamma_a)\tau_1}$$

$$\int\limits_0^{t} d\tau_2 e^{(i\omega_a+\gamma_a)\tau_2}e^{(i(\omega_{ext}-\omega_b)-\gamma_b)(\tau_1-\tau_2)} = \Omega_{Rpl}^2 e^{(i\omega_a-\gamma_a)(t+\tau)}e^{(-i\omega_a-\gamma_a)t}\frac{g^2|S_{SERS}|^2}{(\omega_{ext}-\omega_\sigma)^2}(\overline{n}_v+1)$$

$$\times\int\limits_0^{t+\tau} d\tau_1 e^{(-i\omega_a+\gamma_a+i(\omega_{ext}-\omega_b)-\gamma_b)\tau_1}\int\limits_0^{t} d\tau_2 e^{(i\omega_a+\gamma_a-i(\omega_{ext}-\omega_b)+\gamma_b)\tau_2}$$

$$= \Omega_{Rpl}^2 e^{(i\omega_a-\gamma_a)(t+\tau)}e^{(-i\omega_a-\gamma_a)t}\frac{g^2|S_{SERS}|^2}{(\omega_{ext}-\omega_\sigma)^2}(\overline{n}_v+1) \times\frac{e^{(-i\omega_a+\gamma_a+i(\omega_{ext}-\omega_b)-\gamma_b)(t+\tau)}-1}{\gamma_a+i(\omega_{ext}-\omega_a-\omega_b)-\gamma_b}\frac{e^{(i\omega_a+\gamma_a-i(\omega_{ext}-\omega_b)+\gamma_b)t}-1}{\gamma_a-i(\omega_{ext}-\omega_a-\omega_b)+\gamma_b}$$

$$\simeq \frac{g^2|S_{SERS}|^2\Omega_{Rpl}^2 e^{(i(\omega_{ext}-\omega_b)-\gamma_b)\tau}}{(\omega_{ext}-\omega_\sigma)^2\left((\omega_{ext}-\omega_a-\omega_b)^2+\gamma_a^2\right)}(\overline{n}_v+1) \tag{16.3.8}$$

Analogously, for the term proportional to $e^{(i(\omega_{ext}+\omega_b)-\gamma_b)(\tau_1-\tau_2)}$, we obtain:

$$\Omega_{Rpl}^2 e^{(i\omega_a-\gamma_a)(t+\tau)}e^{(-i\omega_a-\gamma_a)t}\frac{g^2|S_{SERS}|^2}{(\omega_{ext}-\omega_\sigma)^2}\overline{n}_v\int_0^{t+\tau}d\tau_1 e^{(-i\omega_a+\gamma_a)\tau_1}\int_0^{t}d\tau_2 e^{(i\omega_a+\gamma_a)\tau_2}e^{(i(\omega_{ext}+\omega_b)-\gamma_b)(\tau_1-\tau_2)}$$
$$\simeq\frac{g^2|S_{SERS}|^2\Omega_{Rpl}^2 e^{(i(\omega_{ext}+\omega_b)-\gamma_b)\tau}}{(\omega_{ext}-\omega_\sigma)^2\left((\omega_{ext}-\omega_a+\omega_b)^2+\gamma_a^2\right)}\overline{n}_v \tag{16.3.9}$$

Combining Eqs. (16.3.6), (16.3.8), and (16.3.9), we obtain:

$$\left\langle\widehat{a}^\dagger(t+\tau)\widehat{a}(t)\right\rangle=\left\langle\widehat{a}_1^\dagger(t+\tau)\widehat{a}_1(t)\right\rangle+\left\langle\widehat{a}_2^\dagger(t+\tau)\widehat{a}_2(t)\right\rangle$$
$$=|A_p|^2e^{i\omega_{ext}\tau}+\left[\frac{g^2|S_{SERS}|^2\Omega_{Rpl}^2e^{(i(\omega_{ext}-\omega_b)-\gamma_b)\tau}}{(\omega_{ext}-\omega_\sigma)^2\left((\omega_{ext}-\omega_a-\omega_b)^2+\gamma_a^2\right)}(1+n_v(T))\right.$$
$$\left.+\frac{g^2|S_{SERS}|^2\Omega_{Rpl}^2e^{(i(\omega_{ext}+\omega_b)-\gamma_b)\tau}}{(\omega_{ext}-\omega_\sigma)^2\left((\omega_{ext}-\omega_a+\omega_b)^2+\gamma_a^2\right)}n_v(T)\right] \tag{16.3.10}$$

This is Eq. (12.2.32) from the main text.

Problem 2.4
Derive Eqs. (13.1.18)–(13.1.18) from the main text:

$$d\widehat{\sigma}_3/dt+(i\omega_\sigma+\gamma_\sigma)\widehat{\sigma}_3$$
$$=\widehat{I}\left[\left(S_{\omega_P}+S_{\omega_P}^{(g)}\right)e^{-i\omega_P t}+\left(S_{\omega_S}+S_{\omega_S}^{(g)}\right)e^{-i\omega_S t}\right.$$
$$\left.+\left(S_{2\omega_S-\omega_P}+S_{2\omega_S-\omega_P}^{(g)}\right)e^{-i(2\omega_S-\omega_P)t}+\left(S_{2\omega_P-\omega_S}+S_{2\omega_P-\omega_S}^{(g)}\right)e^{-i(2\omega_P-\omega_S)t}\right], \tag{16.4.1}$$

where

$$S_{\omega_P}=\frac{i|\Omega_S|^2\Omega_P}{4(\omega_S-\omega_\sigma)^2}+\frac{i|\Omega_P|^2\Omega_P}{4(\omega_P-\omega_\sigma)^2}+\frac{i|\Omega_S|^2\Omega_P}{4(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)},$$
$$S_{\omega_S}=\frac{i|\Omega_S|^2\Omega_S}{4(\omega_S-\omega_\sigma)^2}+\frac{i|\Omega_P|^2\Omega_S}{4(\omega_P-\omega_\sigma)^2}+\frac{i|\Omega_P|^2\Omega_S}{4(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)},$$
$$S_{2\omega_S-\omega_P}=\frac{i\Omega_P^*\Omega_S^2}{4(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}, \tag{16.4.2}$$
$$S_{2\omega_P-\omega_S}=\frac{i\Omega_S^*\Omega_P^2}{4(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}$$

Solution

The Hamiltonian of the molecule, which interacts with two coherent waves, is

$$\widehat{H}_{\mathrm{S}} = \hbar\omega_\sigma \widehat{\sigma}^\dagger \widehat{\sigma} + \hbar\omega_{\mathrm{v}} \widehat{b}^\dagger \widehat{b} + \hbar g \widehat{\sigma}^\dagger \widehat{\sigma}\left(\widehat{b}^\dagger + \widehat{b}\right) + \frac{\hbar\Omega_P}{2}\left(\widehat{\sigma}^\dagger e^{-i\omega_P t} + \widehat{\sigma} e^{i\omega_P t}\right) + \frac{\hbar\Omega_S}{2}\left(\widehat{\sigma}^\dagger e^{-i\omega_S t} + \widehat{\sigma} e^{i\omega_S t}\right) \tag{16.4.3}$$

The Heisenberg equation of motion for the operators $\widehat{b}$ and $\widehat{\sigma}$ has the form:

$$d\widehat{b}/dt + (i\omega_b + \gamma_b)\widehat{b} = -ig\widehat{\sigma}^\dagger \widehat{\sigma} \tag{16.4.4}$$

$$d\widehat{\sigma}/dt = (-i\omega_\sigma - \gamma_\sigma)\widehat{\sigma} + \frac{i}{2}\left(2\widehat{\sigma}^\dagger \widehat{\sigma} - 1\right)\left(\Omega_P \mathrm{e}^{-i\omega_1 t} + \Omega_S \mathrm{e}^{-i\omega_2 t}\right) - ig\widehat{\sigma}\left(\widehat{b}^\dagger + \widehat{b}\right) \tag{16.4.5}$$

We neglected the noise term in Eq. (16.4.4) because we are interested in the coherent response of the molecular dipole moment.

To solve Eqs. (16.4.4)–(16.4.5), we employ the perturbation theory with the small parameters:

$$\Omega_{S,P}/|\omega_{ext} - \omega_\sigma| \ll 1, \quad g/\omega_\sigma \ll 1 \tag{16.4.6}$$

In the zero order of the perturbation theory, Eqs. (16.4.4)–(16.4.5) are reduced to

$$d\widehat{b}_0/dt + (i\omega_{\mathrm{v}} + \gamma_{\mathrm{v}})\widehat{b}_0 = 0, \tag{16.4.7}$$

$$d\widehat{\sigma}_0/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_0 = 0, \tag{16.4.8}$$

The stationary solutions to these equations are $\widehat{\sigma}_0 = 0$, $\widehat{b}_0 = 0$.

In the first order of the perturbation theory, we obtain the equations:

$$d\widehat{b}_1/dt + (i\omega_{\mathrm{v}} + \gamma_{\mathrm{v}})\widehat{b}_1 = 0, \tag{16.4.9}$$

$$d\widehat{\sigma}_1/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_1 = -i\frac{\Omega_P}{2}e^{-i\omega_P t} - i\frac{\Omega_S}{2}e^{-i\omega_S t}. \tag{16.4.10}$$

Their stationary solutions are

$$\widehat{b}_1 = 0 \tag{16.4.11}$$

$$\widehat{\sigma}_1 = \frac{1}{2}\frac{\Omega_S}{\omega_S - \omega_\sigma + i\gamma_\sigma}e^{-i\omega_S t} + \frac{1}{2}\frac{\Omega_P}{\omega_P - \omega_\sigma + i\gamma_\sigma}e^{-i\omega_P t} \tag{16.4.12}$$

In the second order of the perturbation theory, the system of equations has the form:

$$d\widehat{b}_2/dt + (i\omega_{\mathrm{v}} + \gamma_{\mathrm{v}})\widehat{b}_2 = -ig\widehat{\sigma}_1^\dagger \widehat{\sigma}_1, \tag{16.4.13}$$

$$d\widehat{\sigma}_2/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_2 = -ig\sigma_1\left(\widehat{b}_0^\dagger + \widehat{b}_0\right), \tag{16.4.14}$$

The solutions to this system are

$$\begin{aligned}\widehat{b}_2 \approx \frac{1}{4}\frac{\Omega_S^*\Omega_P}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}\cdot\frac{g}{\omega_P-\omega_S-\omega_\nu+i\gamma_\nu}e^{-i(\omega_P-\omega_S)t}+\\ +\frac{1}{4}\frac{\Omega_P^*\Omega_S}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}\cdot\frac{g}{\omega_S-\omega_P-\omega_\nu+i\gamma_\nu}e^{-i(\omega_S-\omega_P)t}+\\ +\frac{1}{4}\frac{|\Omega_S|^2}{(\omega_\sigma-\omega_S)^2}\cdot\frac{g}{-\omega_\nu+i\gamma_\nu}+\frac{1}{4}\frac{|\Omega_P|^2}{(\omega_\sigma-\omega_P)^2}\cdot\frac{g}{-\omega_\nu+i\gamma_\nu}\end{aligned} \tag{16.4.15}$$

$$\widehat{\sigma}_2(t) = 0 \tag{16.4.16}$$

The corresponding equation for $\widehat{\sigma}_3$ has the form:

$$\begin{aligned}d\widehat{\sigma}_3/dt + (i\omega_\sigma+\gamma_\sigma)\widehat{\sigma}_3 = -ig\widehat{\sigma}_1\left(\widehat{b}_2^\dagger+\widehat{b}_2\right)\\ +i\widehat{\sigma}_1^\dagger\widehat{\sigma}_1\left(\Omega_S e^{-i\omega_S t}+i\Omega_P e^{-i\omega_P t}\right),\end{aligned} \tag{16.4.17}$$

Taking into account explicit expressions for $\sigma_1, \sigma_1^\dagger, \mathrm{b}_2^\dagger, b_2$ (see Eqs. (16.4.12) and (16.4.15)), we arrive at the following equation:

$$\begin{aligned}&d\widehat{\sigma}_3/dt + (i\omega_\sigma+\gamma_\sigma)\widehat{\sigma}_3\\ &= -ig\widehat{\sigma}_1\left(\widehat{b}_2^\dagger+\widehat{b}_2\right)+i\widehat{\sigma}_1^\dagger\widehat{\sigma}_1\left(\Omega_S e^{-i\omega_S t}+\Omega_P e^{-i\omega_P t}\right)\\ &= -ig\left(\frac{1}{2}\frac{\Omega_S}{\omega_S-\omega_\sigma}e^{-i\omega_S t}+\frac{1}{2}\frac{\Omega_P}{\omega_P-\omega_\sigma}e^{-i\omega_P t}\right)\times\left(\frac{1}{4}\frac{\Omega_S^*\Omega_P}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}\right.\\ &\quad\times\frac{g}{\omega_P-\omega_S-\omega_\nu+i\gamma_\nu}e^{-i(\omega_P-\omega_S)t}+\frac{1}{4}\frac{\Omega_P^*\Omega_S}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}\\ &\quad\times\frac{g}{\omega_P-\omega_S-\omega_\nu-i\gamma_\nu}e^{i(\omega_P-\omega_S)t}+\frac{1}{4}\frac{\Omega_P^*\Omega_S}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}\\ &\quad\times\frac{g}{\omega_S-\omega_P-\omega_\nu+i\gamma_\nu}e^{-i(\omega_S-\omega_P)t}+\frac{1}{4}\frac{\Omega_S^*\Omega_P}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)}\\ &\quad\times\frac{g}{\omega_S-\omega_P-\omega_\nu-i\gamma_\nu}e^{i(\omega_S-\omega_P)t}+\frac{1}{2}\frac{|\Omega_S|^2}{(\omega_\sigma-\omega_S)^2}\cdot\frac{-\omega_\nu g}{\omega_\nu^2+\gamma_\nu^2}+\frac{1}{2}\frac{|\Omega_P|^2}{(\omega_\sigma-\omega_P)^2}\\ &\quad\left.\times\frac{-\omega_\nu g}{\omega_\nu^2+\gamma_\nu^2}\right)+\frac{i}{4}\left(\frac{\Omega_S^*}{\omega_S-\omega_\sigma}e^{i\omega_S t}+\frac{\Omega_P^*}{\omega_P-\omega_\sigma}e^{i\omega_P t}\right)\left(\frac{\Omega_S}{\omega_S-\omega_\sigma}e^{-i\omega_S t}+\frac{\Omega_P}{\omega_P-\omega_\sigma}e^{-i\omega_P t}\right)\\ &\quad\times\left(\Omega_S e^{-i\omega_S t}+i\Omega_P e^{-i\omega_P t}\right)\end{aligned} \tag{16.4.18}$$

Further, after multiplying all the terms, we collect the terms that depend on g and multiplied by $e^{-i\omega_S t}$, $e^{-i\omega_P t}$, $e^{-i(2\omega_S-\omega_P)t}$, and $e^{-i(2\omega_P-\omega_S)t}$, and the term that does not depend on g and multiplied by $e^{-i\omega_S t}$, $e^{-i\omega_P t}$, $e^{-i(2\omega_S-\omega_P)t}$, and $e^{-i(2\omega_P-\omega_S)t}$. The result has the form:

$$
\begin{aligned}
&d\widehat{\sigma}_3/dt+(i\omega_\sigma+\gamma_\sigma)\widehat{\sigma}_3=-i\frac{g}{8}\\
&\times\Bigg[\Bigg(2\frac{|\Omega_S|^2\Omega_S}{(\omega_\sigma-\omega_S)^2(\omega_S-\omega_\sigma)}\cdot\frac{-\omega_v g}{\omega_v^2+\gamma_v^2}+2\frac{|\Omega_P|^2\Omega_S}{(\omega_\sigma-\omega_P)^2(\omega_S-\omega_\sigma)}\cdot\frac{-\omega_v g}{\omega_v^2+\gamma_v^2}\\
&+\frac{|\Omega_P|^2\Omega_S}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)(\omega_P-\omega_\sigma)}\cdot\frac{g}{\omega_P-\omega_S-\omega_\mathrm{v}-i\gamma_\mathrm{v}}\\
&+\frac{|\Omega_P|^2\Omega_S}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)(\omega_P-\omega_\sigma)}\cdot\frac{g}{\omega_S-\omega_P-\omega_\mathrm{v}+i\gamma_\mathrm{v}}\Bigg)e^{-i\omega_S t}\\
&+\Bigg(2\frac{|\Omega_S|^2\Omega_P}{(\omega_\sigma-\omega_S)^2(\omega_P-\omega_\sigma)}\cdot\frac{-\omega_v g}{\omega_v^2+\gamma_v^2}+2\frac{|\Omega_P|^2\Omega_P}{(\omega_\sigma-\omega_P)^2(\omega_P-\omega_\sigma)}\cdot\frac{-\omega_v g}{\omega_v^2+\gamma_v^2}\\
&+\frac{|\Omega_S|^2\Omega_P}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)(\omega_S-\omega_\sigma)}\cdot\frac{g}{\omega_P-\omega_S-\omega_\mathrm{v}+i\gamma_\mathrm{v}}\\
&+\frac{|\Omega_S|^2\Omega_P}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)(\omega_S-\omega_\sigma)}\cdot\frac{g}{\omega_S-\omega_P-\omega_\mathrm{v}-i\gamma_\mathrm{v}}\Bigg)e^{-i\omega_P t}\\
&+\Bigg(\frac{\Omega_P^*\Omega_S^2}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)(\omega_S-\omega_\sigma)}\cdot\frac{g}{\omega_P-\omega_S-\omega_\mathrm{v}-i\gamma_\mathrm{v}}\\
&+\frac{\Omega_P^*\Omega_S^2}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)(\omega_S-\omega_\sigma)}\cdot\frac{g}{\omega_S-\omega_P-\omega_\mathrm{v}+i\gamma_\mathrm{v}}\Bigg)e^{-i(2\omega_S-\omega_P)t}\\
&+\Bigg(\frac{\Omega_S^*\Omega_P^2}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)(\omega_P-\omega_\sigma)}\cdot\frac{g}{\omega_P-\omega_S-\omega_\mathrm{v}+i\gamma_\mathrm{v}}\\
&+\frac{\Omega_S^*\Omega_{PP}^2}{(\omega_\sigma-\omega_S)(\omega_\sigma-\omega_P)(\omega_P-\omega_\sigma)}\cdot\frac{g}{\omega_S-\omega_P-\omega_\mathrm{v}-i\gamma_\mathrm{v}}\Bigg)e^{-i(2\omega_P-\omega_S)t}\Bigg]\\
&+\frac{i}{4}\Bigg[\Bigg(\frac{|\Omega_S|^2\Omega_S}{(\omega_S-\omega_\sigma)^2}+\frac{|\Omega_P|^2\Omega_S}{(\omega_P-\omega_\sigma)^2}+\frac{|\Omega_P|^2\Omega_S}{(\omega_S-\omega_\sigma)(\omega_P-\omega_\sigma)}\Bigg)e^{-i\omega_S t}\\
&+\Bigg(\frac{|\Omega_S|^2\Omega_P}{(\omega_S-\omega_\sigma)^2}+\frac{|\Omega_P|^2\Omega_P}{(\omega_P-\omega_\sigma)^2}+\frac{|\Omega_S|^2\Omega_P}{(\omega_S-\omega_\sigma)(\omega_P-\omega_\sigma)}\Bigg)e^{-i\omega_P t}\\
&+\frac{\Omega_S^*\Omega_P^2}{(\omega_S-\omega_\sigma)(\omega_P-\omega_\sigma)}e^{-i(2\omega_P-\omega_S)t}+\frac{\Omega_P^*\Omega_S^2}{(\omega_S-\omega_\sigma)(\omega_P-\omega_\sigma)}e^{-i(2\omega_S-\omega_P)t}\Bigg]
\end{aligned}
\tag{16.4.19}
$$

On the right-hand side, terms proportional to $\exp(-i\omega_S t)$, $\exp(-i\omega_P t)$, $\exp(-i(2\omega_S - \omega_P)t)$, and $\exp(-i(2\omega_P - \omega_S)t)$ appear. These terms play the role of the monochromatic external forces, which cause responses of $\widehat{\sigma}$ at the corresponding frequencies. The response on the frequency ω_S corresponds to stimulated Raman scattering (SRS); responses on the frequencies $2\omega_S - \omega_P$ and $2\omega_P - \omega_S$ correspond to coherent Stokes and anti-Stokes scattering (CSRS and CARS, respectively). In this section, we are interested in the effect of SRS; therefore, in Eq. (16.4.19) we consider only the terms oscillating at the frequency ω_S. As a result, Eq. (16.4.19) takes the form:

$$
\begin{aligned}
&d\widehat{\sigma}_3/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_3 = -i\frac{g}{8} \\
&\times \left(2\frac{|\Omega_S|^2\Omega_S}{(\omega_\sigma - \omega_S)^2(\omega_S - \omega_\sigma)} \cdot \frac{-\omega_v g}{\omega_v^2 + \gamma_v^2} + 2\frac{|\Omega_P|^2\Omega_S}{(\omega_\sigma - \omega_P)^2(\omega_S - \omega_\sigma)} \cdot \frac{-\omega_v g}{\omega_v^2 + \gamma_v^2} \right. \\
&+ \frac{|\Omega_P|^2\Omega_S}{(\omega_\sigma - \omega_S)(\omega_\sigma - \omega_P)(\omega_P - \omega_\sigma)} \cdot \frac{g}{\omega_P - \omega_S - \omega_\mathrm{v} - i\gamma_\mathrm{v}} \\
&\left. + \frac{|\Omega_P|^2\Omega_S}{(\omega_\sigma - \omega_S)(\omega_\sigma - \omega_P)(\omega_P - \omega_\sigma)} \cdot \frac{g}{\omega_S - \omega_P - \omega_\mathrm{v} + i\gamma_\mathrm{v}} \right) e^{-i\omega_S t} \\
&+ \frac{i}{4}\left(\frac{|\Omega_S|^2\Omega_S}{(\omega_S - \omega_\sigma)^2} + \frac{|\Omega_P|^2\Omega_S}{(\omega_P - \omega_\sigma)^2} + \frac{|\Omega_P|^2\Omega_S}{(\omega_S - \omega_\sigma)(\omega_P - \omega_\sigma)} \right) e^{-i\omega_S t}
\end{aligned}
\tag{16.4.20}
$$

Further, we are interested in the case when the frequencies ω_S and ω_P satisfy the condition $\omega_P - \omega_S \simeq \omega_v$. For this reason, on the right-hand side in the first parenthesis, we retain only the term whose denominator contains the expression $\omega_P - \omega_S - \omega_\mathrm{v}$, i.e., the third term in the first parenthesis. Moreover, in experiment, the amplitude of the pump wave is usually much larger than the amplitude of the Stokes wave, $\Omega_P \gg \Omega_S$. Thus, on the right-hand side, in the second parenthesis, we retain only the terms proportional to $|\Omega_P|^2\Omega_S$. Taking into account that $\omega_\sigma \gg \omega_S, \omega_P$ and $\omega_\sigma - \omega_S \simeq \omega_\sigma - \omega_P$, we arrive at the following equation:

$$
\begin{aligned}
d\widehat{\sigma}_3/dt + (i\omega_\sigma + \gamma_\sigma)\widehat{\sigma}_3 = &-i\frac{|\Omega_P|^2\Omega_S}{8(\omega_\sigma - \omega_S)(\omega_\sigma - \omega_P)(\omega_P - \omega_\sigma)} \\
&\times \frac{g^2}{\omega_P - \omega_S - \omega_\mathrm{v} - i\gamma_\mathrm{v}} e^{-i\omega_S t} + i\frac{1}{2}\frac{|\Omega_P|^2\Omega_S}{(\omega_P - \omega_\sigma)^2} e^{-i\omega_S t}
\end{aligned}
\tag{16.4.21}
$$

Equation (16.4.21) has a solution:

$$\widehat{\sigma}_3 = \frac{1}{2}\,\frac{|\Omega_P|^2\Omega_S e^{-i\omega_S t}}{(\omega_\sigma-\omega_P)^2(\omega_\sigma-\omega_S)}\,e^{-i\omega_S t} + \frac{1}{8}\,\frac{g^2}{(\omega_P-\omega_S-\omega_{\rm v}-i\gamma_{\rm v})}\,\frac{|\Omega_P|^2\Omega_S e^{-i\omega_S t}}{(\omega_\sigma-\omega_P)^2(\omega_\sigma-\omega_S)^2} \tag{16.4.22}$$

Note that at the resonance, $\omega_P - \omega_S = \omega_{\rm v}$, expression (16.4.22) reduces to

$$\widehat{\sigma}_3 = \frac{1}{2}\,\frac{|\Omega_P|^2\Omega_S e^{-i\omega_S t}}{(\omega_\sigma-\omega_P)^2(\omega_\sigma-\omega_S)}\,e^{-i\omega_S t} + \frac{1}{8}\,i\frac{g^2}{\gamma_{\rm v}}\,\frac{|\Omega_P|^2\Omega_S e^{-i\omega_S t}}{(\omega_\sigma-\omega_P)^2(\omega_\sigma-\omega_S)^2} \tag{16.4.23}$$

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